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# ALLEN'S
# COMMERCIAL ORGANIC ANALYSIS

## FIFTH EDITION, REWRITTEN, REVISED, RESET

The aim has been to include in the nine volumes of Allen, the organic chemicals and products employed in the arts, manufactures, commerce, medicine, science, etc. It treats upon the properties, modes of analysis, proximate analytical examination; methods for detection and estimation of impurities, adulterations, products of decomposition, etc.

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NOTE: Volume III enlarged over previous edition by 96 pages and 11 illustrations.

**Modern Explosives.** By A. MARSHALL, F. I. C., Kirkee, India. Introductory; Cellulose Nitrates; Examination of Nitrocellulose; Nitrostarch; Nitroglycerin; Separation of Nitro Aromatic Compounds; Picric Acid; Picrates; Dinitrophenol; Nitrotoluenes; Trotyl or T. N. T.; Nitrochlorbenzenes; Nitronaphthalenes; Tetranitromethylaniline (Tetryl); Mercury Fulminate; Gelatinizers and Stabilizers; Diphenylamine; Moisture in Explosives; Analysis of Complex Explosives; Fireworks; Detonators; Abel Heat Test; U. S. Directions for Abel Test; Significance of Heat Tests; Fume Tests; Quantitative Tests; Chemical Methods; Bibliograpy.

36 Illustrations 8vo IX + 732 Pages.

# ALLEN'S
# COMMERCIAL ORGANIC ANALYSIS

## VOLUME IV

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# ALLEN'S COMMERCIAL
# ORGANIC ANALYSIS

A TREATISE ON

## THE PROPERTIES, MODES OF ASSAYING, AND PROXIMATE ANALYTICAL EXAMINATION OF THE VARIOUS ORGANIC CHEMICALS AND PRODUCTS EMPLOYED IN THE ARTS, MANU- FACTURES, MEDICINE, Etc.

WITH CONCISE METHODS FOR

### THE DETECTION AND ESTIMATION OF THEIR IMPURITIES, ADULTERATIONS, AND PRODUCTS OF DECOMPOSITION

## VOLUME IV

Special Characters of Essential Oils; Resins, India-Rubber, Gutta Percha,
Balata, and Allied Substances; The Constituents of Essential Oils,
and Allied Substances; The General Characters and
Analysis of Essential Oils

BY THE EDITORS AND THE FOLLOWING CONTRIBUTORS

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# PREFACE

Although there is more material in this volume than in the corresponding volume of the previous edition, it has been handled by fewer contributors. In this case it seemed better to have "Essential Oils" prepared in two sections only: One discussing the subject from the standpoint of the individual essential oils and the other from that of the various chemical substances themselves, found in essential oils.

As far as practicable, the general methods of analysis applicable to groups of compounds such as the resins or the essential oils, having the same general constituents, are treated in the general discussion, whilst individual peculiarities are treated in the detailed discussion.

This volume has been largely rewritten and therefore contains much new matter. This is particularly true of the sections treating upon general methods of analysis and investigation of Resins, and of the important constituents of Essential Oils. The section on Rubber, as now revised, fully sets forth the best available methods, with only a moderate increase in the size of the section. Certain obsolete or little used methods have been eliminated.

The temperatures quoted are *Centigrade* unless otherwise specified.

The term "optical rotation" in this volume represents the observed angular rotation at $15°$ C. for 100 millimetres of the liquid, the sign $[\alpha]_D$ denoting the specific rotation of the substance for sodium light (D-ray).

As in previous volumes, in the absence of any statement to the contrary, all specific gravities refer to a temperature of $15.5°$ C. compared with water as unity at the same temperature.

Most of the refractive indices have been taken at $20°$ C. and in most cases this is indicated in the test.

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## THE CONSTITUENTS OF ESSENTIAL OILS; AND ALLIED SUBSTANCES

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# THE GENERAL CHARACTERS AND ANALYSIS OF ESSENTIAL OILS

### ERNEST J. PARRY, B. Sc., F. I. C.

# SPECIAL CHARACTERS OF ESSENTIAL OILS

By E. K. NELSON AND G. A. RUSSELL

In the following section some of the important essential oils are described, and methods for their examination, chiefly with a view to the detection of adulteration, are detailed. The physical characters of oils not described in this section will be found included in a table at end of the volume (p. 188).

## Cymbopogon Oils. Indian-grass Oils

The oils of citronella, lemon-grass, palmarosa, ginger-grass, and vetiver or cus-cus are all derived from tropical grasses now referred to the genus *Cymbopogon* which was formerly recognized only as a subgenus.

**Citronella Oil.**—By far the larger portion of the oil in commerce is produced in Ceylon, by distilling the dry grass (*Lana Batu* or *Maha Pengiri*) with steam. The oil is pale yellow to yellowish-brown, and sometimes greenish owing to traces of copper. The parent plant of citronella grass is known as mana grass of which Stapf distinguishes two varieties, *Cymbopogon Nardus, var. Linnæi*, and *C. Nardus var. confertiflorus*. The natives differentiate still further in Ceylon, and the following table illustrates this differentiation, with the character of the various oils themselves.

The Maha-pengiri grass, which is cultivated largely in Java, is *Cymbopogon Winterianus*.

The solubility of both these citronella oils is the same, a clear or only faintly opalescent solution being formed on shaking with 1 to 3 volumes of 80% alcohol. When this clear solution is diluted to 10 volumes with 80% alcohol, no oily drops should separate on standing, though a mere turbidity may be disregarded if previously present. This is known as "Schimmel's test" (see page 2).

| No. | Parent plant | | $d_{15}$ | $\alpha_D$ | Total alcohol % | Geraniol % | Citronellal % |
|---|---|---|---|---|---|---|---|
| | Botanical name (according to Stapf's determination) | Native name | | | | | |
| 1 | C. Nardus, Rendle var. Linnæi, Stapf (typicus) | Maha-naran-pengiri | 0.920 | − 3° 7′ | 51.6 | 27.6 | 24.0 |
| 2 | C. Nardus, Rendle var. Linnæi, Stapf (typicus) | Maha-naran-pengiri | 0.905 | − 6° 32′ | 63.2 | 38.4 | 24.8 |
| 3 | C. Nardus, Rendle var. Linnæi, Stapf (typicus) | Maha-naran-pengiri | 0.912 | + 3° 22′ | 57.2 | 36.2 | 21.0 |
| 4 | C. Nardus, Rendle var. Linnæi, Stapf (typicus) | Heen-naran-pengiri | 0.913 | + 2° 35′ | 43.5 | 24.6 | 18.9 |
| 5 | C. Nardus, Rendle var. Linnæi, Stapf (typicus) | Heen-naran-pengiri | 0.894 | − 3° 20′ | 47.7 | 25.8 | 21.9 |
| 6 | C. Nardus, Rendle var. Linnæi, Stapf (typicus) | Heen-naran-pengiri | 0.909 | + 2° 6′ | 53.5 | 30.0 | 23.5 |
| 7 | C. Nardus, Rendle var. Linnæi, Stapf (typicus) | Light-leaved mana | 0.909 | + 4° 54′ | 56.5 | 38.6 | 17.9 |
| 8 | C. Nardus, Rendle var. Linnæi, Stapf (typicus) | Light-leaved mana | 0.908 | + 3° 30′ | 64.0 | 30.2 | 33.8 |
| 9 | C. Nardus, Rendle var. Linnæi, Stapf (typicus) | Small-leaved mana | 0.906 | + 3° 7′ | 57.0 | 34.4 | 22.6 |
| 10 | C. Nardus, Rendle var. Linnæi, Stapf (typicus) | Small-leaved mana | 0.909 | + 3° 20′ | 56.3 | 36.5 | 19.8 |
| 11 | C. Nardus, Rendle var. Linnæi, Stapf (typicus) | Sour mana | 0.935 | +16° | 35.3 | 16.3 | 19.0 |
| 12 | C. Nardus, Rendle var. Linnæi, Stapf (typicus) | Sour mana | 0.967 | +15° 50′ | 26.9 | 6.3 | 20.6 |
| 13 | C. Nardus, Rendle var. Linnæi, Stapf (typicus) | Very broad-leaved mana | 0.926 | + 1° 31′ | 48.7 | 25.8 | 22.9 |
| 14 | C. Nardus, Rendle var. Linnæi, Stapf (typicus) | Very broad-leaved mana | 0.906 | − 0° 24′ | 64.7 | 36.5 | 28.2 |
| 15 | C. Nardus, Rendle var. Linnæi, Stapf (typicus) | Given as "maha-pengiri," but probably "mana" | 0.912 | − 1° 38′ | 48.6 | 25.5 | 23.1 |
| 16 | C. Nardus, Rendle var. Linnæi, Stapf (typicus) | Given as "maha-pengiri," but probably "mana" | 0.909 | − 2° 18′ | 56.4 | 35.8 | 20.6 |
| 17 | C. Nardus, Rendle var. confertiflorus, Stapf | Glaucous-leaved-mana | 0.913 | +12° 12′ | 46.5 | 29.3 | 17.2 |
| 18 | C. Nardus, Rendle var, confertiflorus, Stapf | Glaucous-leaved-mana | 0.900 | + 4° | 61.2 | 43.7 | 17.5 |
| 19 | C. Nardus, Rendle var. confertiflorus, Stapf | White-stemmed mana | 0.908 | + 1° 27′ | 54.8 | 30.2 | 24.6 |
| 20 | C. Nardus, Rendle var. confertiflorus, Stapf | White-stemmed mana | 0.904 | + 2° 26′ | 58 0 | 24.8 | 33.2 |
| 21 | C. Nardus, Rendle var. confertiflorus, Stapf | Red-stemmed mana | 0.929 | + 6° 19′ | 39.1 | 19.4 | 19.7 |
| 22 | C. Nardus, Rendle var. confertiflorus, Stapf | Red-stemmed mana | 0.909 | + 0° 58′ | 57.0 | 28.9 | 28.1 |
| 23 | C. Nardus, Rendle, closely allied to var. confertiflorus | Lenabatu-pengiri (not genuine) | 0.915 | + 2ᶜ 46′ | 52.0 | 31.1 | 20.9 |
| 24 | C. Nardus, Rendle, closely allied to var. confertiflorus | Lenabatu-pengiri (not genuine) | 0.902 | − 2° 11′ | 63.1 | 39.5 | 23.6 |
| 25 | C. Nardus, Rendle, closely allied to var. confertiflorus | Lenabatu-pengiri (not genuine) | 0.907 | − 0° 6′ | 64.2 | 44.8 | 19.4 |

But it must be remembered that practically the whole of the oil exported in drums from Ceylon is adulterated with petroleum—so as just to pass Schimmel's test. The custom of purchasing on a geraniol standard (*i. e.*, total acetylisable constituents) is rapidly gaining ground.

In order to avoid any uncertainty as to the indications given by Schimmel's test, Parry (*Chem. and Drug.*, 1901, **59,** 142) has pro-

posed the use of a slightly stronger alcohol in the case of those oils which give a turbidity with 80% alcohol.   Some pure oils (generally those of high sp. gr.) give a clear solution with 3 or 4 vols. of 80% alcohol and subsequently a turbid solution on diluting to 10 volumes. In nearly all such cases the use of alcohol of 81 to 83% strength results in a clear solution with 10 vols. of the alcohol.   If small quantities of petroleum are present, however, there is little change in the turbid solution, even if 85% alcohol be employed.

Umney and Swinton have published results showing that the variable composition of commercial citronella oils is probably, at least in part, due to the fact that some distillates are produced by the aid of steam and others by the open-fire method (*Year Book Pharm.*, 1897, 365).

The constituents of Ceylon citronella oil hitherto identified are as follows: citronellal, geraniol, camphene, dipentene, methyl-heptenone, borneol, methyl-eugenol, limonene, thujyl alcohol (?), nerol, geranyl acetate, *d*-citronellyl acetate and butyrate and a sesquiterpene of sp. gr. 0.8643, probably identical with an aliphatic sesquiterpene isolated by Semmler and Spornitz (*Ber.*, 1913, **46**, 4025) from Java citronella oil, and which has the following characters: sp. gr. 0.8489, optical rotation +0° 36′, ref. ind. 1.5325, and b. p. 138–140° at 9 mm. pressure.   Elze (*Chem. Zeit.*, 1913, **37**, 1422) has quite recently isolated about 0.25% of farnesol from this oil.   The Java oil contains geraniol, citronellal, *d*-citronellol, traces of methyl-eugenol, citral, isovaleric aldehyde, *iso*-amyl-alcohol and the sesquiterpene, citronellene, above mentioned.

The following figures may be taken to cover the vast majority of genuine samples.

|                       | Ceylon oil       | Java oil        |
|-----------------------|------------------|-----------------|
| Sp. Gr..............................| 0.898 to 0.920   | 0.884 to 0.900  |
| Optical rotation..................| −7° to −20°      | 0° to −3°       |
| Ref. ind. at 20°...................| 1.4790 to 1.4890 | 1.4650 to 1.4720|
| Total "Geraniol"..................| 57% to 64%       | 83% to 96%      |

The higher sp. gr. of the Ceylon oil is probably due to the greater proportion of methyl-eugenol which it contains.

The methods for the estimation of citronellal and geraniol are fully described on page 601 *et seq.*   The acetylation process when

applied to citronella oil does not express the true proportion of geraniol, as is now generally recognised (p. 519).   But it does give a *relative* figure, and the acetylisable constituents should always be estimated.

Citronella oil is much used as a perfume for cheap toilet soaps, and in consequence is frequently adulterated.   Petroleum (kerosene) is much employed, and fixed oils are sometimes added.   Either adulterant disturbs the ready solubility of the oil in 80% alcohol, petroleum producing a milk-white mixture and after long standing oily drops on the surface of the solution; fixed oils cause a turbid liquid, and eventually oily drops collect at the bottom.   Another difference is that a citronella oil containing fixed oil is not soluble in 80% alcohol in any proportion (1 to 10 volumes), oils containing petroleum are soluble in 2 volumes, but with 10 volumes the milk-white turbidity is produced.

Parry and Bennett have recorded the presence of 20% of alcohol in citronella oil.   The oils containing this also contained other adulterants, the spirit being added to enable the samples to meet Schimmel's test.   Gurjun-balsam oil has been found in adulterated oil of citronella.

Another adulterant is *light resin spirit* found by Parry and Bennett to the extent of 12% and upward in certain oils (*Chem. and Drug.*, 1903, **62**, 88, 408).   Although the exact nature of this adulterant is somewhat doubtful, Parry and Bennett believe it to be either pure light resin spirit or a mixture of this substance with light petroleum spirit.   On fractional distillation at reduced pressure (20 mm.), such adulterated oils gave a fraction (first 10%) having a sp. gr. of 0.822, a rotation of $-26.8°$, a ref. ind. of 1.4490, and b. p. 150° to 160° at the ordinary pressure.   Under similar conditions, Parry and Bennett found normal citronella oils to give a fraction having a minimum sp. gr. of 0.858; opt. rot., $-45°$ (but this is variable); ref. ind. near 1.4600, and not below 1.4570 at 20°.   The solubility of the fraction in 10 volumes of 80% alcohol should be noted.   Pure oils always yield a perfectly soluble fraction, but oils containing notable proportions of resin spirit yield an insoluble fraction. These characteristics, and the reduced rotation of the first 10% distilled, are stated by Parry and Bennett to suffice for detection of the adulterant.

For some time Schimmel's test (p. 2) was regarded as sufficient to detect all likely adulterants, but the discovery of light petroleum

and resin spirits in citronella oils was shown by Parry and Bennett to place the test in a less satisfactory position.  Thus, while some of these adulterated oils give distinct insoluble matter with Schimmel's test, others have been found to contain 20% of the resin-spirit and yet meet the test.  For this reason Schimmel & Co. have described the following modified test (the so-called "Raised Schimmel's test"): 2 tests are made side by side: one exactly as usual in the ordinary Schimmel's test; the other after the addition of 5 % of Russian petroleum to the oil under examination.  Both the original oil and that to which petroleum has been added should be soluble in 80% alcohol as employed, and oily drops should not separate in either case.

*Lemongrass Oil.*—This oil is obtained in the East Indies by distilling, when fresh, the grass *Cymbopogon flexuosus, Stapf.* and in the West Indies by distilling a closely related grass *Cymbopogon citratus.* According to Parry (Parry, E. J. *The Chemistry of the Essential Oils*, 4th Edition, 1921) the latter oil is not frequently met with in commerce today, but according to Stapf (*Bull. Imp. Inst.* **3**, 1903–13), C. citratus is also abundant in the East Indies.

Lemongrass oil is yellow to reddish-brown in colour, with a strong lemon-like odour and taste.  The sp. gr. lies between 0.899 and 0.905 with exceptional instances where the density has ranged from 0.895 up to 0.910.  The opt. rot. lies between the limits of $+1.42°$ to $-5°$, the ref. ind. 1.4825 to 1.4885.  The oil according to Gildemeister and Hoffmann (Gildemeister, E., *The Volatile Oils*, 2nd Ed.) is soluble in 1.5 to 3 vols. of 70% alcohol, and oils of that solubility are obtainable.  The citral content of normal oils vary from 68% to 85% and from 65% to 80% according to whether the bisulphite method (page 520) or the sulphite method (page 521) is employed in the analysis.  When recording analysis or purchasing on a guaranteed aldehyde content the method of analysis should always be mentioned.

The constituents of lemongrass oil are citral, citronellal, *n*-decylic aldehyde, an aldehyde isomeric with citronellal, methyl-heptenone, geraniol, linalol, dipentene and limonene.

**The estimation of citral** in lemon-grass oil is described at length on page 521.  The sulphite method is useful only as giving comparative results between various samples, the figures not being absolutely accurate.  The presence of methyl-heptenone does not interfere with the estimation of citral by this method, since the com-

pound formed with this ketone is decomposed at 100° and the free ketone is measured with the unabsorbed portion of oil.

Lemon-grass oil should contain not less than 70% of citral.   Many samples contain a much larger proportion, but some have suffered partial extraction of this constituent.

The citral content of lemongrass oil decreases with length of storage.   A decrease of from 79 to 68% in three months was observed on a sample of "wet" oil, whereas a "dry" oil decreased from 79 to 74% (Umney, J. C. & Bunker, *S. W. Perfum. and Essential Oil Record*, **4**, (1913) 38).   Likewise Bourbon oil showed a decrease of 18% in citral value in three years, as did also a lemon-grass oil from Cochin (*Perfumery & Essential Oil Record*, 1916, **7**, 95).   It is desirable, therefore, to protect lemongrass oil from light and air and that it should be well dried before storage.

This oil is frequently adulterated, and some of the additions made to increase the value (for instance, *acetone*, found by Parry) are ingenious.   Fixed oils are often added and occasionally petroleum. Either of these latter additions causes a decreased solubility in 70% alcohol, while the sp. gr. is generally disturbed, and in the case of fixed oils these, upon distillation of the lemongrass oil, remain in the distilling flask and are readily recognized.

Citronella oil was found by Parry in certain consignments of lemongrass oil.   The solution of the oil in 70% alcohol quickly became cloudy on cooling, pure oils requiring somewhat prolonged cooling of this solution to produce cloudiness.   Citronellal was readily detected in the sulphite compound separated from the oil.

**Acetone** was found by Parry in some lemon-grass oils of slightly low sp. gr. (0.893).   The apparent percentage of citral was 76. Distillation of such oils at the ordinary pressure gave about 11% of distillate (chiefly acetone) below 60°.

Lemon-grass oil is used in perfumery, and has been employed in the adulteration of lemon oil.   An important use to which it is now put is in the manufacture of *ionone*, the artificial perfume of the violet produced from lemon-grass citral.

Numerous samples of lemon-grass oil from various parts of the world have been examined in recent years.   These, however, are scarcely commercial articles and call for no remarks other than that as cultivation of the lemongrass increases variations in the oil may be expected.

Another volatile oil possessing a lemon grass-like odour is derived from the leaves of a small tree (*Backhousia citriodora*) growing in southern Queensland.  It contains a larger proportion of citral than lemon grass oil, yeilding as high as 94.95%, according to Umney. This oil should not be confused with the oil from *Eucalyptus citriodora*, which contains little or no citral, but consists almost entirely of citronellal.

**Palmarosa Oil.  Indian Geranium Oil.**—This oil, sometimes misnamed Turkish geranium oil, derived from *Cymbopogon martini var. motia* is colourless or light yellow sometimes darkened according to the method of distillation, and sometimes coloured green by copper. It has a characteristic geranium or rose-like odour, and contains a large proportion of geraniol, chiefly free, but from 5 to 15% of esters (geranyl acetate and caproate) are generally present.  In addition, it contains a small quantity of dipentene, and possibly some methylheptenone.  Traces of farnesol and traces of caproic acid as ester are also present.  (Elze, *Chem. Zeit.*, 1910, **34**, 857.)  The free geraniol present ranges from 65 to 95% in pure oils, as estimated by acetylation, while the total geraniol should not be less than 75% and frequently reaches a much higher figure (93%).  The esters present absorb from 3 to 5% of potassium hydroxide.

Schimmel & Co. give the following percentages of geraniol in 4 pure samples:

|   | Combined | Free | Total |
|---|---|---|---|
| 1 | 12.1 | 76.36 | 88.46 |
| 2 | 13.55 | 69.93 | 83.33 |
| 3 | 8.67 | 68.23 | 76.9 |
| 4 | 8.48 | 83.15 | 91.63 |

Pure palmarosa oil has sp. gr. 0.885 to 0.900.  It is but slightly active optically, the range noted being $-3°$ to $+6°$, mostly between $-2°$ to $+1°$.  Ref. ind. from 1.472 to 1.4780; acid value to 3; ester value 12 to 50; total geraniol 65 to 95%.  Solubility in 70% alcohol 1. vol. in 1.5 to 3.0 vols.  Oils with a high geraniol content are soluble in from 3 to 4 vols. and more of 60% alcohol.

Many adulterants interfere with the solubility of the oil, among which are the oils of gurjun balsam and turpentine, and petroleum, fixed oils (especially coconut oil) and cedar-wood oil.  Fixed oils

leave a non-volatile residue.    The ester value and geraniol content are lowered by oil of turpentine, which also lowers the sp. gr., as does petroleum.    Oils containing an admixture of coconut oil frequently partially solidify in a freezing-mixture.    All of them betray their presence by the insolubility of the oil in 70% alcohol.

Palmarosa oil is not related to true geranium oil in any way, but it possesses a similar odour.    It is employed in cheap perfumery, and finds use also as an adulterant of rose otto and of true geranium oil. It is known locally as "Rusa" oil.

**Ginger Grass Oil.**—Oil of gingergrass was formerly regarded as adulterated or inferior palmrosa oil, but it is now known to be a distinct product, derived from *Cymbopogon martini var sofia.*

The known constituents of gingergrass oil are the terpenes dipentene, *d*-α-phellandrene, *d*-limonene, together with heptaldehyde, *i*-carvone, an aldehyde of the formula $C_{10}H_{16}O$, geraniol and α-dihydrocuminic alcohol.

Gingergrass oil has a sp. gr. at 15° of 0.900 to 0.953; opt. rot. +54° to −30°; ref. ind. 1.4780 to 1.4930; acid value up to 6.2; ester value 8 to 29 (rarely to 54.5); ester value after acetylation 120 to 200; soluble in 3 vols. 70% alcohol (usually) but generally becomes cloudy on addition of more alcohol.    Parry [*Parry, E. J.* 1, 85 (4th Ed.)] states some samples do not appear to be soluble in 3 vols. 70% alcohol but require considerably more to effect solution.

Gingergrass oil is so universally subject to adulteration that, at times, it is difficult to obtain a pure sample.    The principal adulterants are turpentine, gurjun balsam oil and mineral oil.    All these lower the solubility and modify the sp. gr.    Gurjun balsam oil also influences the angle of rotation.

**Vetiver Oil.**—This oil is distilled from the roots of *Vertiveria zizanioides* Stapf, formerly known as *Andropogon muricatus.*    It is a viscous oil with a heavy, penetrating odour, and is used to a considerable extent in the manufacture of perfumes of the oriental type. The roots are known in India by the name of Khas-Khas or cus-cus.

The oil distilled in Europe from the dried imported root has the following characters:

| | |
|---|---|
| Sp. gr. 15°.................................. | 1.015 to 1.040 |
| Opt. rot................................... | +25° to +37° |
| Ref. ind. to 20°........................... | 1.5220 to 1.5270 |
| Acid value................................ | 27 to 65 |
| Ester value............................... | 9.8 to 23 |
| Ester value after acetylation.............. | 130 to 158 |

It is soluble in 1 to 3 volumes of 80% alcohol, additional alcohol usually causing turbidity.

The oil distilled in Réunion from the fresh imported root has the following characters:

| | |
|---|---|
| Sp. gr 15°...................... | 0.982 to 1.020 rarely over 1.050 |
| Optical rotation................. | +10° to +38° |
| Ref. index...................... | 1.5150 to 1.5285 |
| Acid value..................... | 4.0 to 20 |
| Ester value.................... | 5 to 20 |
| Ester value after acetylation........ | 103 to 150 |

It is soluble in 1 to 3 volumes of 80% alcohol, additional alcohol usually causing turbidity.

Fiji and Seychelles vetiver oils do not differ materially from the above described oil.

Puran Singh (*Chem. and Druggist*, 1914, **2,** 51) has examined the oil distilled in India from Indian-grown roots, and his results suggest that in the distillation of the roots a small amount of resin is carried over, and that if the oil be freed from this by careful redistillation, the resulting oil is lævorotatory. Seventy-five grm. of oil were carefully steam-distilled and about 65 grm. of oil resulted. The residue was a dark red resinous mass, which was extracted with alcohol. About 9.4 grm. of a dark-red resin of a brilliant fracture were obtained. It softened at 65°, and completely melted at 70°. It gave the following constants:

| | |
|---|---|
| Sp. gr. at 30°................................... | 1.132 |
| Acid value....................................... | 46.92 |
| Saponification value.............................. | 111.02 |
| Ester value...................................... | 64.28 |
| Iodine value (Hübl, after 18 hours)[1]............... | 268.20 |
| Optical rotation calculated on 10 c.c. of the solid resin... | +488.04 |

[1] Approximately; because the solution had to be made too dilute for observation, owing to the very dark colour of the resin.

The redistilled oil, which was of a yellowish-brown colour and quite transparent, gave the following constants:

| | |
|---|---|
| Sp. gr. at 15°......  ............................. | 1.011 |
| Opt. rot. in 100-mm. tube......................... | −30.65 |
| N$_D$ 20°.......................................... | 1.5165 |
| Acid value....................................... | 10.5 |
| Saponification value.............................. | 80.1 |
| Ester value...................................... | 69.6 |
| Saponification value after acetylisation.............. | 132.8 |
| Iodine value (Hübl, after 18 hours)................ | 194.4 |
| Soluble in 2 parts of 80% alcohol. | |

The above constants are different from those already recorded by various observers. This difference may be due to the elimination of the resin from the oil by redistillation; at least in optical rotation it is mainly due to this cause. The angle of rotation of the oil in this case is about $-31°$, while all observers have recorded for vetiver oil a rotation of $+25°$ to $+40°$. The optical rotation of the resin is $+488.4°$. Taking the proportion of the oil to resin, as it is in this case, to be 8 : 1, the optical rotation calculated on the mixture of resin and oil comes to $+34°$. It seems that the dextrorotation of the oil is due to the small proportion of *Khas-Khas* resin. This will also have its effect on other constants. It is not known whether the constants of this oil, as recorded by other observers, were determined on redistilled oil or on the first distillate. If on the latter, then the constants of this resin-free oil will in all cases be different from those already published. This has yet to be ascertained.

The statements recorded with regard to the composition of vetiver oil vary considerably and cannot always be harmonized.

Genvresse and Langlois isolated from this oil a hydrocarbon $C_{15}H_{24}$ which they termed *vetivene* and an alcohol, *vetivenol*, $C_{15}H_{26}O$, an ester of this alcohol, and an acid of the formula $C_{15}H_{24}O_2$. Semmler and his colleagues (*Ber.* 1912, **45,** 2347) have more recently shown that vetivenol has the formula $C_{15}H_{24}O$, and the acid $C_{15}H_{22}O_2$. For the differences between the alcohol and esters present in vetiver oils of different origins, the original paper should be consulted.

Schimmel and Company report finding castor oil (Schimmel & Co.'s *Semi-Annual Report* 1916, p. 60) and glycerin acetate (Schimmel & Co.'s *Ber.* 1922, 77) as adulterants of vetiver oil. In the case of samples containing castor oil all the constants were found to vary considerably from the normal, especially the ester value. The oil gave a clear solution at first with light petroleum, but on further addition of the solvent became turbid, and after a time oil separated out. Vetiver oil is readily soluble in light petroleum, whereas castor oil is insoluble. Glycerin acetate was identified by its solubility in water, its sp. gr. (1.1654 at 15°) and its high sap. value (671.6)

## Almond Oil

Essential oil of bitter almonds is a commercial product of considerable importance, as it is used to a large extent in the preparation of flavouring essences.

The true bitter almond oil is obtained by distillation from the seeds of *Amygdalis communis* var. *amara,* the ordinary bitter almond. But as the kernels of the peach and apricot yield an oil which is indistinguishable from that of the almond, it is certain that much of the almond oil of commerce is really derived from peach and apricot kernels. Hence the remarks made here apply to all three oils indiscriminately.

The oil does not exist as such in the seeds, but is produced by the action of the enzyme emulsin on the glucoside amygdalin, under the influence of water. Without discussing the question of intermediate products, the action taking place results, in the main, in the formation of benzaldehyde and hydrocyanic acid as follows:

$$\underset{\text{amygdalin}}{C_{20}H_{27}NO_{11}} + 2H_2O = \underset{\text{benzaldehyde}}{C_7H_6O} + HCN + \underset{\text{glucose}}{2C_6H_{12}O_6}$$

The natural oil, therefore, contains hydrocyanic acid and is highly poisonous. The commercial article is, therefore, usually deprived of hydrocyanic acid and sold as "Ol. amygdalæ essent. sine acido prussico (S.A.P.)."

**Composition.**—This oil consists principally of benzaldehyde (with or without hydrocyanic acid) and a little benzaldehyde-cyanhydrin, $C_5H_6(CH)(OH)CN$, formed by the interaction of the aldehyde and the acid.

**Characters.**—The sp. gr. of the natural oil varies between 1.045 and 1.070 at 15°. It is optically inactive or, at most, very faintly dextrorotatory, up to $+0°$ 10'. Its ref. ind. is from 1.5320 to 1.5440. The oil is soluble in 2 vols. of 70% alcohol.

Hydrocyanic acid is detected by shaking the oil with water, and then adding to the water minute quantities of ferrous and ferric chlorides, and then a solution of caustic potash. On adding hydrochloric acid a blue colour or precipitate is formed if hydrocyanic acid be present. To estimate the hydrocyanic acid, 1 grm. should be dissolved in 5 c.c. of alcohol and 50 c.c. of water added. An ammoniacal solution of silver nitrate is then added, and the whole well shaken. The liquid is then acidified with nitric acid, and the silver cyanide is collected, washed and weighed as silver, after ignition. Four parts of silver correspond to one of hydrocyanic acid.

*U. S. P. Assay for Hydrocyanic Acid.*—Dissolve 15 grm. of crystallized magnesium sulphate in enough distilled water to measure 100

c.c.    Add 5 c.c. of this solution to 40 c.c. of distilled water, then add 5 c.c. of N/2 sodium hydroxide and 2 drops of 10 per cent potassium chromate solution, and titrate the solution with N/10 silver nitrate to the production of a permanent reddish tint.    Pour this mixture into a 100 c.c. flask containing about 1 grm., accurately weighed, of Bitter Almond Oil, mix well, and titrate again with N/10 silver nitrate until a red tint, which does not disappear on shaking, is reproduced.    Conduct this titration as rapidly as possible.

One c.c. of N/10 silver nitrate corresponds to 0.0027 grm. of hydrocyanic acid.

If deprived of hydrocyanic acid, the oil has a sp. gr. 1.050 to 1.055, and a ref. ind. of 1.5420 to 1.5460 at 20°.    It boils principally at 179° and is soluble in 1 to 2 volumes of 70% alcohol.    Nitrobenzene has been found as an adulterant of this oil, but is rarely used now. Its sp. gr. is about 1.200 and its odour is characteristically coarse. It can be detected with certainty by boiling the oil with a little acetic acid and iron filings.    The nitrobenzene is reduced to aniline, which is distilled off and a few drops of chlorinated lime solution added to the distillate; the characteristic violet colour results if aniline be present.    The usual adulterant, however, is synthetic benzaldehyde.    This can be detected, chemically, only if it contains traces of chlorine, which the lower grades do, having been made by a chlorination process.    To detect chlorine, a pure filter paper is saturated with the oil and placed in a small porcelain dish, standing in a larger one, and a beaker whose sides are moistened with distilled water is inverted over the smaller dish after the paper has been lighted.    After the paper is burned, the beaker is washed out with a few drops of distilled water, the liquid filtered, and the filtrate tested for chlorides in the usual manner.    Heyl (*Apoth. Zeit.* 1912, **27,** 49) recommends the following method:

1 to 2 grm. of chlorine-free calcium hydroxide are stirred up with a glass rod in a small porcelain dish with 10 to 15 drops of benzaldehyde, the mixture is then covered with a thin layer of calcium hydroxide and slowly brought to a red heat.    After cooling, the contents of the dish are poured into a beaker, 5 to 6 c.c. of water are carefully added, and the mixture is faintly acidified with nitric acid.    The solution is then filtered through chlorine-free filter paper or glass-wool and tested for chlorine with silver nitrate. Rupp (*ibid*), prefers the following test:

A copper wire, or, better still, a strip of copper wire-netting 0.5 cm. in width (about 1 mm. mesh) is twisted at one end into a narrow spiral shape, forming a roll about the diameter of a large pea. This roll is repeatedly drawn through a non-luminous flame in order to oxidise the surface of the copper and to remove any yellow or green coloration. When cool, the roll is dipped into the benzaldehyde under examination and is then exposed to the flame for a moment in order to inflame the benzaldehyde. When the benzaldehyde is burnt off (not in the flame) the roll is again applied to the top of the flame. If there is a green coloration, chlorine is present.

*U. S. P. Assay for Benzaldehyde.*—Dissolve about 3 c.c. of freshly redistilled phenylhydrazine in about 60 c.c. of alcohol and titrate 25 c.c. of this solution, which must be freshly prepared, with $N/2$ hydrochloric acid, using 1 drop of Methyl Orange T. S. as indicator. To about 1 grm. of Bitter Almond Oil, accurately weighed, add 25 c.c. of the phenylhydrazine solution and allow the mixture to stand 30 minutes. Add 1 drop of Methyl Orange T. S., and acidify the mixture by adding a measured excess of $N/2$ hydrochloric acid. Filter the mixture, and wash the precipitate with small portions of distilled water until the washings cease to redden moistened blue litmus paper. Then titrate the excess of hydrochloric acid in the filtrate with $N/2$ potassum hydroxide. Subtract the number of c.c. of $N/2$ hydrochloric acid neutralised from the number of c.c. of $N/2$ hydrochloric acid used in titrating 25 c.c. of the phenyl-hydrazine solution; the difference multiplied by 0.053 gives the weight of benzaldehyde.

## Angelica Oil

This oil is present in all parts of the herb *Angelica officinalis* (*Angelica Archangelica*), but is mainly distilled from the roots. According to Schimmel & Co., however, the finest oil is that distilled from the fruit (seed).

Angelica-root oil, when distilled from the fresh material, is light yellow or reddish with an aromatic odour and a pungent taste. By exposure to air and light, it becomes of a yellow or brownish colour and on long standing the oil deposits a crystalline substance. Giordani found this compound to melt at 74° to 77°, and to have the composition $C_{22}H_{62}O_5$. The ref. ind. of the oil is about 1.4800.

The following table shows the properties of angelica oil, according to the character of the plant used for distillation:

| Material used | Sp. gr. of oil at 15° | Opt. rot. | Constituents |
|---|---|---|---|
| Fresh root........ | 0.854 to 0.905 | +18 to +36° | Methyl-ethyl-acetic acid; dextrophellandrene; oxypentadecylic acid. |
| Dried root........ | Up to 0.918 | ............. | ...................... |
| Whole herb....... | 0.869 to 0.890 | +8 to +25° | |
| Fruit (seed)....... | 0.856 to 0.890 | +10 to +13° | Phellandrene; methyl-ethyl-acetic acid; oxy-myristic acid. |

Schimmel & Co. (*Report*, April, 1911, **20**) give the following values for angelica oil distilled by themselves from various parts of the plant.

| Oil from | Sp. gr. at 15° | Rotation | Ref. index at 20° | Acid No. | Ester No. |
|---|---|---|---|---|---|
| Leaves................ | 0.8550 | +28° 2′ | 1.4778 | 0.5 | 17.6 |
| Leaves................ | 0.8697 | +22° 8′ | 1.4804 | 1.3 | 22.6 |
| Leaves................ | 0.8767 | +20° 11′ | 1.4832 | 1.6 | 21.1 |
| Root................. | 0.8733 | +28° 23′ | 1.4808 | 2.5 | 25.9 |
| Seed................. | 0.8623 | +12° 12′ | 1.4868 | 1.1 | 18.1 |

In Scientific and Industrial Bulletin Series 4, 1921, No. 4, 33, Roure-Bertrand Fils report an angelica root oil distilled by themselves as having the following characters.

Sp. gr. at 15° (corr.) 0.8907, opt. rot. at 18° + 6° 42′, acid value 7.20, ester value 45.07, soluble in 2 vols. or more of 90% alcohol.

3 samples of angelica-root oil examined by Haensel showed sp. gr. of 0.854 to 0.856 and opt. rot., +38° to +39°. An oil from the dried root had a sp. gr. of 0.875, and an opt. rot. of +23.6°.

It was shown by Beilstein and Weigand in 1882 (*Ber.*, 1882, **15**, 1741), and by Naudin in 1883 (*Bull. Soc. Chim.*, [2], 1883, **39**, 406), that oil of angelica-root contains terpenes, of which dextrophellandrene has since been recognised by Schimmel & Co. (*Rep.*, April, 1891). The oil (root-oil?) distils, according to Parry, between 170° and 310°. Pinene and cymene are possibly also constituents

of this oil, and the presence of one or more sesquiterpenes has been inferred from the high b. p. (250°) of the heavier fractions.

Ciamician and Silber (*Ber.*, 1896, **29**, 1811) have isolated from angelica-root oil 2 crystalline substances, which are stated to have the constitution of anhydrides of oxyacids. Angelica oil also contains methyl-ethyl-acetic acid and oxypentadecylic acid, $C_{15}H_{30}O_3$, the latter substance crystallising from ether in groups of needles, m. p. 62° to 63°. As has been pointed out by Schimmel & Co., it is worthy of note that the oxypentadecylic acid present in angelica-root oil is replaced by oxymyristic acid, a lower homologue, in the oil from angelica-fruit. Angelica-root oil finds its chief employment in the manufacture of liqueurs.

**Japanese angelica-root oil** is the product of the plants *Angelica anomala* and *A. refracta*. The sp. gr. of the oil at 15° is 0.905 to 0.915, ref. ind. at 20° 1.4911, acid value 10.6 and ester value 40. It has an acrid odour, but resembles musk to some extent. At a temperature of 10°, crystals separate from the oil, which solidifies to a pasty mass at 0°. These crystals melt at 62° to 63°, and have all the characters of a fatty acid, possibly oxypentadecylic acid.

The b. p. is between 170° and 310°, the high-boiling fractions are bluish-green.

### Anise Oils

True anise oil is obtained from the fruit of *Pimpinella anisum*. The oil of star-anise, obtained from the fruit of *Illicium verum*, constitutes the bulk of the oil of anise found in commerce. Both oils are recognised in the British Pharmacopœia (1898) and in the United States Pharmacopœia (8th Rev.). An oil produced from *Seseli Harveyanum*, known in some parts of Australia as "anise oil," has more of the appearance and flavour of fennel oil.

Anise oil (from *Pimpinella anisum*) contains anethole, methyl-chavicol and possibly aniseketone, with small quantities of anisic aldehyde and anisic acid. W. A. Tilden states that dextropinene is also present. In addition to anethole and methylchavicol, oil of star-anise contains *l*-limonene, phellandrene in 3 modifications, safrol, the ethyl-ether of hydroquinone, *p*-cymene, cineole and dipentene. According to Tardy, terpineol is also present.

Bouchardat and Tardy (*Ct. r.*, 1896, **122**, 198) found a sample of Russian anise oil to contain small quantities of aniseketone

and fenchone. The sample examined by them, however, was not a normal oil, since it had a m. p. of 10° and was dextrorotatory. It is most probable, therefore, that the sample in question was adulterated with fennel oil.

The *physical characters* of the 2 forms of anise oil are practically identical. Both are pale yellow and somewhat viscous. The British Pharmacopœia (1898) directs that it should congeal when stirred at temperatures between +10° and +15°, and should not become liquid again below +15°. The sp. gr. at 20° should be 0.975 to 0.990. The United States Pharmacopœia (9th Rev.) gives the sp. gr. at 25° as 0.978 to 0.988; the ref. index, 1.544 to 1.560 at 20° C. A normal oil should not congeal at a temperature lower than +15°, the usual range being about +15° to +18° or 19°.

The solidifying point of ainseed oil is a factor of the highest importance. The fact that the oil can exist in the liquid condition at a temperature much below its congealing point is immaterial, since crystallisation can be induced by sowing the oil with a crystal of anethole, or by skilful stirring with the thermometer. If the oil, in a narrow test-tube, be cooled to about 9° or 10°, and a crystal of anethole added, or crystallisation induced by stirring, the thermometer will rapidly rise as crystallisation sets in, and the maximum temperature, which a little experience will readily determine, indicates the true congealing point. In the best oils this will be at least 15°, and congealing points below this indicate inferior oils, or oils from which anethole has been deliberately extracted.

According to Pancoast and Kebler (*Amer. J. Pharm.*, 1901, **73,** 356), pure anise oils having a low congealing point are sometimes met with. They are obtained from a mixture of immature seed and leaf oils, and are known as "Flower Oils." According to the United States Pharmacopœia (9th Rev.), absence of oils containing phenols may be proved by the following tests: An alcoholic solution of the oil should be neutral to litmus-paper, and should not assume a blue or brownish colour on the addition of a drop of ferric chloride test solution. The absence of alcohol is shown by shaking a definite measure of the oil with water in a narrow cylinder. Spermaceti is said to have been used as an adulterant of anise oil. If present in notable amount, spermaceti would lower the sp. gr. and raise the m. p. The solubility of the oil in alcohol would also be reduced. Pure anise oil should dissolve to a perfectly clear solution in 3 parts

of 90% alcohol. Oxidised oils are more soluble, completely oxidised samples dissolving in rectified spirit in all proportions.

The presence of methyl-chavicol, the isomer of anethole, in anise oil, is shown by the action of boiling alcoholic potassium hydroxide on the anethole free oil. The b. p. of the liquid is raised, and on cooling, a further large quantity of anethole crystals is produced.

The constituents of oil of anise gradually undergo oxidation on keeping the oil, a rise in its sp. gr. being produced, while the m. p. is lowered. Oxidised oils show the presence of notable quantities of anisic aldehyde when shaken with sodium hydrogen sulphite solution (25%), whereas fresh oils give no such reaction. Oils examined by this test should be kept at 20° to prevent crystallisation of anethole.

The presence of petroleum oil in aniseed oil is very easily detected by the lowering of the sp. gr., the lowering of the congealing point and ref. index, and the insolubility in even large quantities of 90% alcohol, when petroleum oil separates and can be examined and identified.

A number of samples have of recent years been found on the market which have either been adulterated with such an oil as camphor oil or from which large quantities of anethole have been abstracted; see Parry (*Chemist and Druggist*, 1910, **77**, 687), Umney (*Perf. and Ess. Oil Record*, 1910, **1**, 236), Jensen (*Pharm. J.*, 1910, **85**, 759) and Durrans (*Perf. and Ess. Oil Record*, 1911, **2**, 60). It is still a question of doubt as to which form of adulteration had been adopted, but Parry recommends dividing the oil into the following fractions: the first = 10%, the three following = 25% each, and the residue = 15%. The following tables show the melting point and ref. index of a normal oil and one suspected by Parry of being adulterated by the addition of such an oil as heavy camphor oil, and the same figures for a normal oil and an oil from which anethole had purposely been abstracted, as illustrating Messrs. Schimmel & Co.'s views that the adulteration has been due to abstraction of anethole.

The figures in the following tables for normal oils will be found useful in judging aniseed oils which are at all doubtful, apart from whether the adulteration is by addition of a foreign oil or by the abstraction of anethole.

PARRY

| No. | Amount of fraction | Normal star anise oil (m. p. 18°) | | Suspected star anise oil (m. p. 12.5°) | |
|---|---|---|---|---|---|
| | | M. p. | $n_{D_{20}}$ to 21° | M. p. | $n_{D_{20}}$ to 21° |
| 1 | 10% | 8° | 1.5316 | −3° | 1.5125 |
| 2 | 25% | 18° | 1.5500 | 15° | 1.5419 |
| 3 | 25% | 20° | 1.5540 | 17.5° | 1.5500 |
| 4 | 25% | 20° | 1.5591 | 18° | 1.5521 |
| 5 (Residue) | 15% | 15° | 1.5522 | 11° | 1.5467 |

SCHIMMEL & CO.

| No. | Amount of fraction | Normal star anise oil (sol. p. 16.5°) | | The same oil after abstraction of part of its anethole (sol. p. 10.1°) | |
|---|---|---|---|---|---|
| | | Sol. p. | $n_{D_{20}}^{°}$ | Sol. p. | $n_{D_{20}}^{°}$ |
| 1 | 10% | 7 5$^c$ | 1.53279 | under 0° | 1.50326 |
| 2 | 25% | 15.7$^c$ | 1.55125 | 8.1° | 1.53885 |
| 3 | 25% | 18.9$^c$ | 1.55866 | 14.5° | 1.55342 |
| 4 | 25% | 19.4$^c$ | 1.55980 | 15.2° | 1.55723 |
| 5 (Residue) | 15% | 7.5$^c$ | 1.56079 | under 0° | 1.55505 |

The 2 oils are slightly lævorotatory, usually about −1° to −3°. This figure is a valuable indication of the purity of anise oils, since their adulteration with fennel oil (or its stearoptene) causes them to show dextrorotation. According to E. Dowzard, some samples of pure anise oil show slight rotation, from +0.03° to +0.7°. This is due to the presence of fenchone, which in the case of adulteration with the stearoptene of fennel oil is retained to a sufficient extent in the stearoptene to cause the product to be more or less dextrorotatory, according to the amount of adulterant present.

Petroleum is sometimes added to anise and star-anise oils. This adulterant causes the oils to be less soluble in alcohol, and lowers the sp. gr., but the m. p. will not be greatly modified. For the estimation of petroleum, the oil may be heated with concentrated sulphuric acid. A residue so obtained consists of petroleum. J. C. Umney

found from 37 to 56% of this adulterant in anise oils. The separated petroleum had a sp. gr. of 0.835.

J. C. Umney (*Chem. and Drug.*, 1899, **54,** 323) considers that the differences in the physical characters of star-anise oils are caused by distillation from raw materials, oils in some parts of China being produced from the leaves and twigs of the star-anise. Parry (*Chemistry of Essential Oils*) favours the view that the differences observed in the commercial oils of anise are not due to the cause described by Umney, but to the fact that the flowers or very early fruits of the plant (removed to allow the remaining fruits to mature to better advantage) are distilled, yielding an oil containing a lower percentage of anethol. Parry examined an oil of this description with the following results: Sp. gr., 0.9916; rotation, +0.3°; solidifying-point, 12°. Umney found that the oil distilled from the leaves had a sp. gr. of 0.9878, and a rotation of +1°. The oil, however, remained fluid even at 8°. By fractional distillation, the oil was found to be rich in anise aldehyde, which usually only occurs in partially or wholly oxidised oils of anise and star-anise. It is probable that the presence of anisic aldehyde in star-anise oil is the cause of the difference in odour between oil of anise and star-anise.

The oils of anise are said to be distinguishable by the following colour test: A saturated solution of hydrochloric acid gas, when added to the oil, gives with anise oil a deep blue, and with star-anise oil, a yellow or brown.

According to J. C. Umney, the so-called "Australian anise oil" has a sp. gr. of 0.914, and an opt. rot. of +14°. It does not become crystalline at 4°. The oil appears to resemble fennel oil more than ordinary oil of anise.

The physical constants and characters of other unimportant varieties of anise oil are described in the table on page 189. A false aniseed from *Illicum religiosum* has been found to yield an oil with a sp. gr. of 1.006, containing eugenol, cineole, safrole, and several terpenes. A so-called anise-bark oil possesses a sp. gr. of 0.969, and consists chiefly of methyl-chavicol.

**Estimation of Anethole.**—The value of oil of anise depends upon its contents of anethole. The proportion of this constituent may be approximately estimated by cooling the oil to a low temperature, and after crystallisation has taken place, pressing the crystals between blotting-paper, and weighing the anethole thus obtained

The amount of anethole may also be ascertained by fractionally distilling the oil, and collecting the fraction coming over between 225° and 235° separately (anethole boils at 232°). The measure of this fraction corresponds very nearly to the content of anethole. Good samples of anise oil generally contain at least 85% of anethole, and the amount should not be less than 80%.

## Bay Oil

This oil, which has frequently been described as being obtained from the leaves of *Myrcia acris*, is, according to E. M. Holmes (*Pharm. J.* [3], 1891, **21**, 837), the product of *Pimenta* (*Eugenia*) *acris*. Both the fresh and the dried leaves have been employed in the distillation of this oil.

Oil of bay is not official in the British or the United States Pharmacopœia, but was in the 7th revision (1890) of the latter. The sp. gr. of the oil ranges from 0.965 to 0.985, being usually about 0.970. Parry (*Chemistry of Essential Oils*) gives the normal sp. gr. of the oil as from 0.965, to 1.01, rarely 1.02. Oils of higher sp. gr. should be regarded with suspicion, being possibly adulterated with oil of pimento or cloves.

The rotation of bay oil should not exceed $-2°$. Adulteration with oil of turpentine will alter this figure considerably.

The constituents of bay oil arranged quantitatively are; eugenol, myrcene, chavicol, methyl eugenol, methyl chavicol, phellandrene and citral.

Bay oil suffers adulteration with several oils, chiefly those of cloves pimento, and turpentine. Clove and pimento oils may be detected by the high sp. gr. and by the following test, directed by the United States Pharmacopœia (1890): If to 3 drops of the oil contained in a small test-tube 5 drops of concentrated sulphuric acid are added, and after the tube has been corked, the mixture allowed to stand for 30 minutes, a resinous mass will be obtained. On adding to this mass 4 c.c. of diluted alcohol, vigorously shaking the mixture, and gradually heating to boiling, the liquid should remain nearly colourless, especially not becoming a red or purplish-red.

Turpentine oil, when present as an adulterant, may be detected in the first fraction of the distilled oil of bay by means of the nitroso-chloride reaction for pinene (page 429) which, according to Power and Kleber, is not present in pure bay oil.

When freshly distilled, bay oil is easily soluble in 90% alcohol. On keeping, its solubility becomes slightly lessened.

The phenolic constituents of bay oil (eugenol and chavicol) are present in considerable proportion, and an estimation of them is valuable. For this, Thoms' process, as described on page 502, is perhaps the most accurate. By this method the proportion of phenolic constituents in genuine bay oil ranges from about 59 to 65%.

Schimmel & Co. report two samples from the Fiji Islands with phenol content of 23% and 24%, respectively, due probably to some manipulation in the manufacture (*Report*, Oct., 1909, **27**).

Bay oil finds its chief employment in perfumery, notably in the manufacture of bay rum.

**California bay oil** is in every respect different from the true oil of bay. The Californian oil is obtained by the distillation of the leaves of *Umbellularia californica*, a tree commonly known as the mountain-laurel, sassafras laurel, or Californian olive tree. The oil is a light yellow liquid, having the following characters:

| | |
|---|---|
| Sp. gr. | 0.935 to 0.950 |
| Opt. rot. | $-22°$ to $-24°$ |
| Acid value | about 5 |
| Ester value | about 5 |
| Ester value after acetylation | about 50 |

It is soluble in 1.5 to 2.5 volumes of 70% alcohol. This oil contains eugenol, $l$-$\alpha$-pinene, safrole, methyl-eugenol, and about 40 to 60% of *umbellulone*, a ketone of sp. gr. 0.950 at 20°, optical rotation $-36°$ 30′, ref., index 1.48325, and b. p. 219–220°. It forms a semi-carbazone melting at 240°–243° (Power & Lees, *Trans.*, 1904, 85, 629, also 1906, 89, 1104,–1907, 91, 271 & 1908, 93, 252).

The sweet bay, *Laurus nobilis*, yields an essential oil having a specific gravity of 0.915 to 0.932 at 15°, $\alpha_D - 15°$ to $-22°$ $N_D$ at 20° 1.4670 to 1.4775, acid value 1 to 3, ester value 20 to 50, ester value after acetylation 36 to 96. Soluble in 1 to 3 vols. of 80% alcohol,—some oils, French especially, soluble in 3 to 10 vols. of 70% alcohol.

It contains $\alpha$-pinene, cineole, $l$-linalol, geraniol, eugenol and methyleugenol together with small amounts of free acetic, isovaleric and isobutyric acids and acetic, valeric and caproic acids in the form of esters as well as a monobasic acid $C_{10}H_{14}O_2$ m. p. 146–147°.

A volatile oil obtained from the fruits of the same tree differs from the leaf oil but slightly.

## Bergamot Oil

This oil is obtained by expression of the fresh peel of the ripe fruit of *Citrus aurantium*, subspecies *Bergamia*. It is greenish, has a pleasant odour and bitter taste. Rectification deprives the oil of its tint, but the product thus produced is much inferior in quality to the undistilled, the esters being considerably reduced in amount (12 to 15 % or less).

The green tint is probably due to chlorophyl. Gildemeister and Hoffmann, however, state that copper is the cause (*The Volatile Oils*, Vol. III, p. 61).

The sp. gr. ranges from 0.881 to 0.886, and in some seasons to 0.888. The distilled oil has a sp. gr. of 0.865 to 0.880. The undistilled oil has a rotation of $+8°$ to $+22°$, but rarely over $+18°$; in some oils rotations as low as $+5.4°$ and as high as $+24°$ have been observed. Many oils are too dark for observation in the 100 mm. tube, and a shorter tube must be employed. The ref. index lies between 1.464 and 1.468, acid value 1.0 to 4.0, a fixed residue of 4.5 to 6.0 % [Sap. value of this residue 160 to 200], and esters as linalyl acetate 34 to 42%.

Freshly expressed oil of bergamot deposits a white, odourless, and tasteless substance known as *bergaptene*. Bergaptene crystallises in needles having the composition $C_{12}H_8O_4$, and melting at 188°. It is the mono-methyl-ether of a dihydrooxycoumarin, or the inner anhydride of bergaptenic acid. On fusing bergaptene with potassium hydroxide, phloroglucol is formed. In addition to the solid constituent, bergamot oil contains dextrolimonene; dipentene (?) *l*-α-pinene, *l*-camphene, bisabolene, dihydrocuminic alcohol, nerol, terpineol, linalol, and linalyl acetate (30 to 42%). Octylene, and acetic acid are also said to be present. The odour is much richer than is that of linalyl acetate alone, and therefore other odoriferous constituents, as yet unknown, exist in the oil. Bergamot oil gives no reaction with Schiff's reagent; unlike orange and lemon oils, it contains no aldehydic body.

According to Charabot (*Bull. Soc. Chem.*, [3], 1899, **21,** 1083), the linalol first produced in the fruit is largely converted into ester, during ripening, by the free acetic acid present, while a small amount

of the alcohol is dehydrated, producing terpenes.  Schimmel & Co. have shown that the proportion of linalyl acetate increases as the fruit ripens.  The following figures illustrate this (*Rep.*, April, 1896): Oil from unripe fallen fruits, 25% esters; from unripe plucked fruits, 33 to 34%; from average ripe fruits, 37%; and from somewhat over-ripe fruits, 44% of esters (linalyl acetate).

Most genuine oils show an ester-content of from 34 to 42%, rarely 45%.  Some pure oils occasionally contain only 30% of linalyl acetate, but this low figure should be regarded with suspicion. Within limits, the value of the oil, which is chiefly used for per-fumery, depends upon the percentage of esters it contains.  For this reason, it is important to bear in mind that the presence of fatty oils and resins (colophony, etc.), adulterations frequently practised, will increase the apparent content of esters.

The presence of the waxy constituents in bergamot oil (bergaptene, etc.) causes it to leave a considerable residue on evaporation at 100°, which residue, in the case of genuine oils, ranges from 4 to 6%.  A known weight of the oil (5 grm.) is heated on a boiling water bath until of constant weight and the odour has completely disappeared. The residue is cooled and weighed.  Published analyses show that this residue always contains a small amount of linalyl acetate (1 to 2%).  If more than 6% of residue remains, the sample is probably adulterated, and should be examined for the presence of fatty oils and resins by ascertaining the saponification value.  In the case of oils adulterated with turpentine oil, oil of orange, or distilled berga-mot oil, the residue may be appreciably less than 4.5 or even less than 4%.  A soft, green, homogeneous residue, not exceeding 6%, is obtained in the case of genuine oils.  When pure, the oil is usually soluble in half its volume of 90%, and in 2 volumes of 80%, alcohol.  The presence of fatty oils (except castor oil) interferes with this solubility.

Besides adulteration with fatty oils and resins, bergamot oil suffers adulteration from oils of turpentine, lemon, and orange, and from distilled bergamot oil (obtained by rasping the peel of injured fallen fruits and distilling the product with water).  Oils of turpentine, lemon, and orange decrease the sp. gr. solubility, fatty residue, and the proportion of esters, while lemon and orange oils raise the opt. rot.  The sp. gr. is increased, on the other hand, by the addition of fatty oils, cedar-wood oil, and gurjun balsam.  Synthetic esters

and lemon terpenes are frequently added together to bergamot oils. An addition of distilled bergamot oil lowers the ester-content and the residue non-volatile at 100°. Fractional distillation should be carried out on all oils suspected to contain oil of turpentine and added terpenes.

The principal adulteration of bergamot oil today is by the addition of artificial esters, together with a neutral substance such as lemon terpenes. The detection of these is fully described under "*Esters*" (on pages 603, 604 *et seq*).

The differences observed in the process of fractional saponification are given under "Esters" on page 604.

Schimmel and Co. have recently pointed out some new adulterants, phthalic acid esters (probably diethyl phthalate) (*Report* 1915 and 1919); triacetin (*Report* 1916) and an anthranilate (*Report* 1918).

S. Gulli (*Chem. and Drug.*, 1901, **59,** 383) has described a new adulterant of bergamot oil, which is prepared by treating oil of turpentine with hydrochloric acid gas to saturation (pinene hydrochloride?). This preparation can be added to bergamot oil to the extent of about 10% without materially altering the constants of the oil or interfering greatly with the ester value (1 to 2% lower). Gulli recommends that in the case of doubtful samples, several grm. of the oil be saponified with alcoholic potassium hydroxide, the liquid evaporated to dryness and the residue ignited. The aqueous solution of the residue should then be tested for the presence of chlorides with silver nitrate.

An inferior oil is obtained from the peel of unripe or damaged fruit. It is brownish-green, has not a very fragrant odour, and contains about 20 to 25% of esters. A sample examined by G. Fabris showed 25.5% of linalyl acetate, and had a sp. gr. of 0.885; opt. rot. at 20°, +9.5°; residue at 100°, 2.70%, containing 1.75% of linalyl acetate. Other investigators examined oil from unripe fruit report sp. gr. 0.8789 to 0.8833; opt. rot. between +7° and +18.6° and an ester content of 26.7 to 33.5%.

**Oil of bergamot leaves** is rarely obtained pure. It is sometimes used as an adulterant of orange oils. It has a sp. gr. of 0.882 to 0.886, a rotation of +8° to +22°, ref. index 1.4654 to 1.4660 and is soluble in an equal volume of 90% alcohol. It contains 32 to 34% of esters (calculated as linalyl acetate), including methyl anthranilate.

The so-called *oil of wild bergamot* (from *Monarda punctata* and *M. fistulosa*) is stated by Braudel and Kremers to contain thymoquinone and hydrothymoquinone. In addition, the oil from *M. punctata* contains cymene, thymol, and dextrolimonene; while that from *M. fistulosa* contains cymene, carvacrol, and limonene.

## Buchu Oil

The oil distilled from buchu leaves is employed to some extent in medicine. The species usually found in commerce are *Barosma betulina, B. crenulata*, and *B. serratifolia*.

Diosphenol, $C_{10}H_{16}O_2$, is the most characteristic constituent of the oil, occurring to a considerable extent in that from *B. betulina*, whilst only to a small extent in that of *B. serratifolia*. It is a crystalline solid, m. p. 83° and b. p. 232°. It is a cyclic keto-phenol and is also known as buchu-camphor. The terpenes, limonene and dipentene are present and also *l*-menthone. The oils of the three species above mentioned have the following characters:

|  | *B. betulina* | *B. crenulata* | *B. serratifolia* |
|---|---|---|---|
| Sp. gr. .............. | 0.937–0.970 | 0.9364 | 0.918–0.961 |
| Rotation........... | −14° to −48° | −15.3° | −12° to −36° |
| Ref. index........ | 1.4740 to 1.4870 | 1.4800 | ................. |

The oils from *Barosma pulchella* and *B. venusta* have also been examined, but are not commercial articles (*Schimmel's Report*, Apr., 1909 and April, 1910, *Pharm. J.*, 1913, **90**, 60).

## Calamus Oil

This oil is used, especially on the Continent, as a flavouring material in the preparation of certain types of beers, liqueurs, etc. The European oil is distilled from the rhizome of *Acorus calamus*, whilst the Japanese oil is probably derived from *Acorus spurius*.

Russian calamus oil contains α-pinene, camphor, a sesquiterpene, calamene (having a sp. gr. 0.922, opt. rot. +5° and ref. index

1.5057) and an alcohol $C_{15}H_{24}O$, which is termed *calamenenol*. (Semmler and Spornitz, *Ber.*, 1913, **46**, 3700.)   Traces of eugenol and heptylic acid are also present.   Japanese calamus oil contains a small amount of methyl-eugenol.   European calamus oil has a sp. gr. 0.958 to 0.970, opt. rot. $+9°$ to $+35°$; ref. index 1.5000 to 1.5080, acid value 0 to 3; ester value 5 to 20, and ester value after acetylation 30 to 55.   It is soluble in practically any quantity of 90% alcohol.   Japanese calamus oil has a sp. gr. 0.970 to 1.995, opt. rot. $+7°$ to $+25°$, ester value about 4, ester value after acetylation, 17.

## Cajuput Oil

This oil, which is official in the British Pharmacopœia (1914) and in the United States Parmacopœia (9th Rev.), is distilled from the leaves of several varieties of *Melaleuca*, chief of which are *M. cajeputi* and *M. minor*.   Many other species of this plant produce oils very similar to the official oil (*e. g., M. uncinata, M. acuminata, M. viridiflora*, etc.

The British Pharmacopœia describes cajuput oil as green or bluish-green, with an agreeable, camphoraceous odour, and an aromatic, bitter camphoraceous taste.   It has a sp. gr. of 0.919 to 0.930. When 10 c.c. of the oil are mixed with 4 to 5 c.c. of syrupy phosphoric acid in a vessel surrounded by a freezing mixture, and then pressed strongly in a piece of calico between folds of blotting paper, the pressed cake, decomposed by warm water in a graduated vessel, yields an oily layer, which, on cooling to $15.5°$ measures not less than 4.5 c.c. (presence of not less than 45% cineole).

The U. S. Pharmacopœia (9th Rev.) describes cajuput oil as having a sp. gr. of 0.912 to 0.925 at $25°$ and being soluble in 1 part of 80% alcohol.   The oil should be lævorotatory (not more than $-4$) and should be free from heavy metals.   In the 8th revision the oil was required to contain at least 55% of cineole (by volume) when assayed by the phosphoric acid process, the phosphate being decomposed by warm water and the resulting cineole measured (see page 56).

Some foreign pharmacopœias (*e. g.*, Italian and Japanese) allow a lower sp. gr. limit than 0.922.   The average cajuput oil differs very little from the British Pharmacopœia limits, although of recent

years the sp. gr. of many pure oils has slightly decreased (to 0.918) owing to a lowered cineole content. Cajuput oil oxidises on exposure to air, the small quantities of butyric, valeric, and benzoic aldehydes being converted into the corresponding acids. The slightly acid reaction of crude cajuput oil is probably due to saponification of the terpenyl acetate and to the above-mentioned oxidation of the aldehydes. Exposure of the oil to light causes polymerisation.

The ref. index of cajuput oil is about 1.4650 to 1.4710, and it normally contains up to 65% cineole.

The sp. gr. of cajuput oil is lowered by adulteration with turpentine oil. Oils containing less than the normal amount of cineole will also show a low sp. gr.

The bluish-green of cajuput oil is chiefly due to traces of copper. The rectified oil is colourless.

Cineole is the chief constituent; $\alpha$-terpineol, terpinyl acetate, and 1 or more terpenes are also present of which $l$-$\alpha$-pinene has been identified. The varieties differ in certain respects from each other in properties and composition. Some (*M. leucadendron*, etc.) contain several fatty compounds, such as butyric and valeric aldehydes. Bertrand (*Bull. Soc. Chim*, [3], 1893, **9**, 432) found that *M. viridifolia* gave an oil (known as "Essence of Niaouli") similar in odour to cajuput oil, and containing cineole, $\alpha$-terpineol, valeric and benzoic aldehydes, valeric acid and terpineol valerate, dextropinene and lævolimonene, (?) and a sulphur compound.

Cajuput oil is generally slightly lævorotatory, ranging from 0° to $-4°$. The oil from *M. acuminata*, however, is stated to have an optical rotation of $-15°$.

Cineole is best estimated by the process described on page 55. Oils of good quality yield 60 to 65%, and 50 to 55% should be fixed as the minimum limit. As already stated, the United States Pharmacopœia (8th rev.) required cajuput oil to contain at least 55% by volume of cineole. Eucalyptus oil is sometimes added to cajuput oil which has been deprived of a portion of its cineole. Fixed oil and petroleum are also said to be used as adulterants of cajuput oil. Oil of good quality should give 60% of distillate between 175° and 185°.

The following characters of the oils from several species of *Melaleuca* are given.

| | Sp. gr. | Opt. rot. | Ref. ind. | Principal constituents |
|---|---|---|---|---|
| *M. acuminata*... | 0.892 | −15.3° | ............... | Cineole |
| *M. bracteata*... | 1.032 to 1.036 | −1.4° to 3.1° | 1.5325 to 1.5350 | Methyl eugenol (70%) |
| *M. decussata*.... | 0.938 | ............... | ............... | ............... |
| *M. ericifolia* ... | 0.899 to 0.902 | dextrogyrate | ............... | Cineole |
| *M. genistifolia*.. | 0.8807 | +32.7° | 1.4702 | *d*-α-pinene (80 to 90%) |
| *M. gibbosa*...... | 0.9138 | +4.5° | 1.4703 | Cineole (61 p.c.) |
| *M. leucadendron* Broad leaf.... | 1.0019 | −3.75° | 1.5250 | Methyl eugenol (78%) |
| Narrow leaf.. | 0.9056 | −0.35° | 1.4794 | ............... |
| *M. linarifolia*... | 0.9129 | +2.5° | 1.4741 | Terpenes |
| *M. Maideni*.... | 0 9199 to 0.9234 | −0.7° to 4.2° | 1.4744 to 1.4800 | Cineole (26 to 39%) |
| *M. minor*....... | 0.917 to 0.930 | −1° to −4° | 1.4650 to 1.4710 | Cineole (65%) |
| *M. nodosa*...... | 0.8984 | +11.6° | 1.4689 | *d*-Pinene and cineole |
| *M. pauciflora*... | 0.9302 | +3.3° | 1.4921 | Sesquiterpene |
| *M. smithii* ..... | 0.8815 to 9.003 | 5.8° to 11.8° | 1.4806 to 1.4824 | ............... |
| *M. thymifolia*... | 0.9134 | +2.1° | 1.4665 | Cineole (53 p.c.) |
| *M. trichostachya* | 0.9144 to 0.9150 | +2.3° to 3.1° | 1.4636 to 1.4655 | Cineole (80 p.c.) |
| *M. uncinata*.... | 0.9211 to 0.9259 | +7.2° to 7.5° | 1.4760 to 1.4788 | Cineole |
| *M. viridiflora*... | 0.908 to 0.929 | −1° to +1° | 1.4723 | Cineole (35 to 60%) |

## Caraway Oil

Caraway oil is obtained by the distillation of the fruit (seed) of *Carum Carvi*. It is a colourless or pale yellow oil, which gradually darkens in colour on keeping. It has a spicy taste.

German "light oil of caraway," also sold under the misleading title "rectified caraway oil," is merely the terpene obtained as a by-product in the manufacture of carvone. It has a sp. gr. of about 0.850 and an opt. rot. exceeding +100°. It is largely employed in soap perfumery.

Oil of caraway consists essentially of dextrolimonene and carvone, $C_{10}H_{14}O$ (see page 565) and, in addition, dihydrocarvone, carveol, dihydrocarveol and a small amount of a base possessing a narcotic odour. It is to the carvone that the value of caraway oil is chiefly due. On this account many of the oils of commerce have been partially or wholly deprived of their carvone, which latter commands a high price and is official in certain pharmacopœias. Such inferior oils can be detected by their lowered sp. gr.

Pure carvone has a sp. gr. of 0.963 to 0.966. Commercial "carvone" is often sold having a sp. gr. from 0.933 to 0.944. It is thus merely fractionated caraway oil. Schimmel & Co. have noted the presence of alcohol (about 5%) in such samples of commercial "carvone."

The British Pharmacopœia directs that oil of caraway should have a sp. gr. of 0.910 to 0.920. According to Schimmel & Co., normal oil of caraway may have a sp. gr. of 0.907 (generally, 0.908 to 0.918). J. C. Umney, however, regards 0.910 as being the lowest allowable limit.

According to the investigations of Schimmel & Co., the oil from the young caraway plant is rich in limonene, but poor in carvone. From the riper material, an oil richer in carvone and poor in limonene is obtained. These observations go to show that the terpene is first formed in the plant, and that the oxygenated constituent is subsequently produced from the terpene.

The opt. rot. of oil of caraway is stated in the British Pharmacopœia, 1914, as 75° +82° and the United States Pharmacopœia (9th Rev.) gives the limits +70° to +80° at 25°. The rotation of pure oils ranges from above +70° to +85°, the mean of these figures being the average rotation of the oil. The refractive index is given in the British Pharmacopœia at 1.4850 to 1.497 at 25°, whereas Parry gives 1.484 to 1.489.

Caraway oil is soluble in 8 volumes of 80% alcohol (United States Pharmacopœia, 9th Rev).

A useful method for the valuation of oil of caraway is the fractional distillation of the oil. Genuine oils will show the largest fractions between 170° and 180° (which contains the whole of the limonene and should not exceed 25%) and 220° and 230° (which contains the carvone and should not be less than 40 to 50%). At least 40% of oil of caraway should distil above 200°.

The carvone in caraway oil can be estimated by the Burgess method, and according to the U. S. P. (10th Rev.) the oil must contain not less than 50% by volume of carvone.

J. Henderson (*Pharm. J.*, [4] 1909, **23,** 610) reports a case of adulteration of caraway oil with castor oil. The sp. gr. of the sample corresponded with the requirement of the B. P. The opt. rot. was +69.7°. The solution with 10 volumes of 80% alcohol was turbid, and an estimation of carvone showed 29%. After fractional distillation 16% of castor oil was detected in the residuum.

Gildemeister and Hoffmann (*The Volatile Oils*) state that alcohol is often used as an adulterant of both caraway oil and carvone, creating the impression that the oil is very soluble; hence they recommend that all samples be tested for alcohol.

## Cardamon Oil

Cardamom oil is obtained from the seeds of *Elettaria cardamomum* and named from the district where produced.

Of these, the principal are those known as Ceylon-Malabars and Ceylon-Mysores. The fruit known as "Ceylon wilds" is derived also from a variety of the same plant. Siam cardamom is the fruit of *Amomum cardamomum*. Terpinyl acetate is an important constituent of the oil, as well as free terpineol and cineole. The following are the characters of the various oils:

|  | *Elettaria cardamomum* | Ceylon wilds | *Amomum cardamomum* |
|---|---|---|---|
| Sp. gr.................... | 0.923–0.944 | 0.895–0.906 | 0.905 at 42° |
| Rotation................. | +24° to +47° | +12° to +15° | +38° |
| Ref. ind................. | 1.4620–1.4670 | ............. | ............. |
| Acid value.............. | to 4 | 1 to 3 | 0.8 |
| Ester value............. | 94–150 | 25–70 | 14–18.8 |
| Solubility in 70% alcohol... | 1 in 2 to 5 vols. | Turbid | Turbid |

This oils is used to a certain extent in flavouring cakes, sauces and other food products.

## Cassia and Cinnamon Oils

Cassia oil is an oil largely employed in the perfuming of cheap soaps, etc. It is distilled from the leaves, twigs and other parts of *Cinnamomum cassia*, a native of Cochin China. The cinnamon oil of commerce is obtained from the bark of *Cinnamomum zeylanicum*, a native of Ceylon. The leaves of this tree also yield an essential oil, which is a commercial article.

**Cassia Oil.**—The principal constituent of this oil is cinnamic aldehyde, small quantities of a terpene, cinnamic esters, *o*-methylcoumaric aldehyde and cinnamic acid being also present. It is customary to grade cassia oils on the market as 70–75, 75–80, and 80–85%, these values indicating the cinnamic aldehyde content. But as pure oils may, and probably usually do, contain from 85 to 90% or even more, it has become a recognised custom to standardise the lower grade oils with resin, so that a 70–75% oil will usually contain 71%, and an 80–85% oil 81% of cinnamic aldehyde.

A pure cassia oil has a sp. gr. 1.055 to 1.072, opt. rot. −1° to +6°, ref. index, 1.6020 to 1.6060, and acid value 6 to 16, rarely to 20. It is easily soluble in 2 volumes of 80% alcohol.

The cinnamic aldehyde should be determined in a cassia flask, 5 c.c. of oil and a hot 30–35% solution of sodium hydrogen sulphite being used. The flask is kept in a boiling water-bath until the whole of the crystals formed are dissolved, the flask being well shaken at frequent intervals. The unabsorbed oil is then forced into the neck of the flask by adding more of the solution and, when cold, the oil is read off, the difference being calculated as cinnamic aldehyde. It is probable that this process gives slightly too high results, whilst the use of neutral sodium sulphite gives results about 3 to 4% lower. It has become an established trade custom, however, to return all results for this oil by the bisulphite process.

The influence of added resin is to raise the acid value of the oil considerably and to cause the oil to leave a high distillation residue. Cassia oils free from resin do not give appreciable precipitates with a saturated solution of lead acetate in alcohol.

The following is the best method of using the lead acetate test, and from the figures quoted (*Perf. and Ess. Oil Record*, 1914, **7**, 264) it will be seen that the higher the lead precipitate, the higher the acid value, and consequent percentage of added resin.

5 grm. of the oil are dissolved in 20 c.c. of 70% alcohol, and 10 c.c. (or more if necessary) of a saturated solution of lead acetate are added. The precipitate is collected on a tared Gooch filter (packed with ignited asbestos) and thoroughly washed with 70% alcohol. The filtrate should be tested with more of the lead acetate solution and any further precipitate filtered off. The precipitate is dried at 100° to constant weight. Results obtained on prepared oils were as follows:

1. Cassia oil, containing 10% resin gave 10.6% lead ppt.
2. Cassia oil, containing 15% resin gave 15.2% lead ppt.
3. Cassia oil, containing 20% resin gave 19.7% lead ppt.

The determination of the acid value of cassia oil, suggested by Yates (*Perf. and Ess. Oil Record*, 1912, 83) cannot be relied upon to indicate exactly the proportion of added resin, on account of the natural variation in the acid values of the oil and resin respectively, and one should hesitate to place reliance on this factor as a means

of judging the percentage of added resin, although it is significant that oils with a high aldehyde content have low acid values.

The following are typical examples of the results obtained:

|  | ALDEHYDE CONTENT | ACID VALUE | LEAD PPT. |
|---|---|---|---|
| 1. Cassia oil free from resin................... | 92 | 6 | nil. |
| 2. Cassia oil free from resin................... | 88 | 13 | nil. |
| 3. Cassia oil containing resin.................. | 82 | 27 | 10.1 |
| 4. Cassia oil containing resin.................. | 73 | 29 | 10.1 |
| 5. Cassia oil containing resin.................. | 72 | 23 | 10.6 |

An approximate estimation of added resin may be obtained by distilling 50 grm. in a small tared Würtz flask and stopping the distillation when the temperature reaches 280°. The residue should not exceed 10%, rarely over 8%, so that any excess may be regarded as resin.

**Cinnamon Bark Oil.**—Although the greater part of the world's supply of this oil comes from Ceylon, a certain amount is distilled on a small scale in other countries, and Seychelles cinnamon oil has recently been carefully examined. Cinnamic aldehyde is the constituent present in largest quantity, but as this oil contains less aldehyde than cassia oil, whilst its odour is far sweeter and more delicate, it is obvious that much of the perfume value lies in the non-aldehydic portion of the oil. The oil contains, in addition, eugenol, methyl-amyl ketone, benzaldehyde, pinene, phellandrene, cymene, nonylaldehyde, cumic aldehyde, hydrocinnamic aldehyde, linalol, linalyl esters, and caryophyllene.

For slight differences in the composition of Seychelles cinnamon oil see Schimmel's Report, April, 1913, 42. According to most authorities, pure cinnamon oil has a sp. gr. 1.020 to 1.040, but Hill (*Chem. and Drug.*, 1910, **76,** 959) and Umney and Bennett (*Perf. and Ess. Oil Record*, 1910, **1,** 169) consider that a lower sp. gr., from 0.994 to 1.022 is normal for pure cinnamon oil. Schimmel & Co. consider that these low sp. gr. are due to abnormal distillation, a certain amount of the aldehyde being oxidised and lost in the distillation. The oil is faintly lævorotatory, up to −1°, and has a ref. index 1.5850 to 1.5910. It contains from 55 to 65% of cinnamic aldehyde (or according to Hill, Umney and Bennett, *loc. cit.*, between 50 and 60%); it should not contain more than 5–10% (rarely more than 6%) of eugenol, as determined by absorption with 5% potassium hydroxide solution. It is soluble in 2 to 3 volumes of 70%

alcohol. The principal adulterants are clove leaf oil and synthetic cinnamic aldehyde.

**Cinnamon leaf oil** is distilled from the leaves of *Cinnamomum zeylanicum*. It closely resembles clove oil, containing from 70 to 90% of eugenol. Small quantities of cinnamic aldehyde and terpenes are present.

The pure oil has a sp. gr. 1.044 to 1.065, opt. rot. −0° 15′ to + 2° 20′; ref. index 1.5310 to 1.5400, and eugenol value from 70 to 90%.

## Camphor Oil

Camphor oil which has been known since early antiquity, is obtained by distilling all parts of the tree *Cinnamomum camphora*.

The oil is obtained as a secondary product, camphor being the primary product. True camphor oil, therefore, should contain as one of its constituents all the camphor obtained in the distillation. In practice, however, the camphor is entirely or partially removed, and the residuum is known as camphor oil. The process of distillation and refining of camphor has been repeatedly described in the literature on the subject, to which the reader is referred for detailed information.

Camphor oil is an exceedingly complicated mixture of hydrocarbons and oxygenated constituents.

The following are the constituents of *normal* camphor oil, only a limited number of which are present in the fractions known commercially as camphor oil.

| | |
|---|---|
| (1) Acetaldehyde. | (13) α-terpineol. |
| (2) *d*-α-pinene. | (14) Citronellol. |
| (3) Camphene. | (15) Safrol. |
| (4) *d*-fenchene. | (16) Δ′-menthenone-3. |
| (5) β-pinene. | (17) Carvacrol. |
| (6) Phellandrene. | (18) Cumic alcohol. |
| (7) Cineole. | (19) Eugenol. |
| (8) Dipentene. | (20) Bisabolene (sesquiterpene). |
| (9) *d*-limonene. | (21) Cadinene. |
| (10) Borneol. | (22) Caprylic acid. |
| (11) Camphor. | (23) An acid $C_9H_{16}O_2$. |
| (12) Terpinenol. | (24) A blue oil. |

In addition to the above compounds, which are given in the order of their boiling points, Semmler and Rosenberg (*Ber.* 1913, **46**, 768) have isolated a sesquiterpene which they term *sesquicamphene* (sp.

gr. 0.9015 at 20°, opt. rot. +3°, and ref. index 1.5006), and a sesquiterpene alcohol, which they name *sesquicamphenol*. A diterpene, $C_{20}H_{32}$, which has been named *α-camphorene*, of sp. gr. 0.8870 at 20° and b. p. 178° under 6 mm., was also isolated.

K. Kafuku (*Pharm. Zentralh.*, 1916, **57**, 683–99) showed the presence of lauric acid. The oil examined by Kafuku contained also a compound $C_{14}H_{26}O_2$, probably the lactone of an aliphatic hydroxy acid, and a tricyclic sesquiterpene alcohol. Piperonylic acid was found in the higher boiling fractions, but may have been formed during distillation by the oxidation of safrol.

Camphor oil appears on the market in various forms varying in character according to the treatment it has undergone and the substances which have been removed thereby. Therefore it is impossible to set up scientific standards by which the oils can be judged. It is usually valued on the basis of its sp. gr., which gives a good indication of its general quality. In order to obtain the value of a given sample it must be completely analysed. The following are the general types of oil found in commerce.

1. Crude camphor oil. This is the oil remaining after the removal of the crystalline camphor. It varies in colour from light yellow to brownish. Sp. gr. 0.950 to 0.958. According to Gildemeister and Hoffman this oil is fractionated in Japan into white oil, red oil and camphor.

2. White camphor oil. It consists of the lower boiling portions and contains principally terpenes with small quantities of cineole. Sp. gr. at 15° 0.870 to 0.910 but rarely over 0.885.

3. Red or black camphor oil. It consists of those portions of the oil boiling higher than camphor and contains safrol, phenols and sesquiterpenes. Sp. gr. at 15° mostly between 1.000 and 1.035.

The oils 2 and 3 above are further fractionated, mainly in Europe and the United States, into safrole and two by-product oils, light camphor oil and heavy camphor oil. The properties of these oils vary in a similar manner and from the same causes as does the original oil.

The light camphor oil has a sp. gr. 0.860 to 0.900, rarely above 0.885. B. p. 175° to 200° or above. It is used as a substitute for turpentine in the manufacture of varnishes, and it resembles turpentine in its general characteristics. It is also used in printing establishments for cleaning types, electroplates, etc.

Heavy camphor oil has a sp. gr. at 15° of about 0.950, b. p. 270° to 300°. It is used in the varnish industry, for perfumery, soap, shoe polish, hoof ointments and for hiding the odour of mineral oils, etc. The safrole obtained on redistilling and fractionating white and red camphor oil is often marketed as "artificial sassafras oil."

A blue camphor oil, which is obtained at a b. p. of about 300°, has a sp. gr. at 15° of about 0.955. It is used similarly to heavy camphor oil.

For the estimation of *camphor* in camphor oil, H. Löhr (*Chem. Zeit.*, 1901, **25**, 292) proceeds as follows: At least 300 grm. of the oil is fractionated, the distillate below 195°, and those between 195°–220° and above 220°, being collected separately. The second fraction, which contains the whole of the camphor, is kept in a freezing mixture for 1 hour, when the camphor is filtered off, wrapped in filter-cloth and then in filter-paper, and pressed for $\frac{1}{2}$ hour. The cake of camphor thus obtained is wrapped in fresh filter-paper and again pressed for fifteen minutes, and is then weighed. The mother-liquor from which the camphor was previously separated is next redistilled, and the fraction at 205° to 220° frozen and treated as before. Five distillations are necessary to obtain all the camphor from the original fraction containing it.

*Camphor Leaf Oil.*—Camphor oil distilled from the leaves varies in composition according to the locality where grown and to the condition and maturity of the leaves. It is usually permeated with a mass of crystalline camphor. The remaining oil, after the removal of the camphor, resembles ordinary crude camphor oil with the notable exception that it contains no safrole.

*Camphor Root Oil.*—Camphor oil distilled from the roots of the camphor tree is rich in crystalline camphor. It contains safrol.

Owing to the method now employed in Formosa of utilizing the whole of the tree for camphor production, leaf and root oils are without doubt mixed indiscriminately with oils from the tree wood.

## Cedar-wood Oil

This oil is obtained from several varieties of cedar, but the oil commonly known under this name, the oil of red cedar-wood, is prepared by the distillation of the wood of *Juniperus virginiana*. The supply comes from many parts of North America, and the oil is

often distilled from the waste wood-shavings from the manufacture of lead-pencils, cedar chests, and cedar lumber. A much inferior oil is sometimes prepared from the condensed vapours of the drying chambers containing the cedar-wood, but the product is devoid of the good odour and other properties of he true cedar-wood oil.

Oil of cedar-wood is a colourless, yellow, or often brownish, thickish oil, with a mild persistent odour. The sp. gr. ranges from about 0.940 or 0.945 to 0.960. It is always lævorotatory, ranging from $-25$ to $-47$. It has a high ref. index (about 1.505 at 17°), and for this reason is much used in connection with oil-immersion lenses. It is soluble in alcohol with difficulty, requiring usually from 10 to 20 parts of 90% alcohol for solution.

When distilled from very old wood, it contains a considerable quantity of *cedrol*, or cedar-camphor. Schimmel & Co. do not consider that this constituent is an essential one in normal cedar-wood oil, but that it is formed when the oil is kept under some conditions. Only small proportions of cedrol are present in cedar-wood oil.

**Cedrol,** $C_{15}H_{26}O$, was obtained from cedar-wood oil, in 1841, by Walter (*Ann.*, 1841, **39,** 247). It forms, when pure, silky crystals with a pleasant aromatic odour. It melts at 78° to 80°.

Besides cedrol, there are present in this oil the sesquiterpene cedrene, (see page 451) cedrenol and pseudocedrol.

Good samples of cedar-wood oil should not contain more than about 10% of the crystalline cedrol (cedar-camphor). Parry obtained, by the examination of 4 genuine samples, 2.32, 2.21, 2.13, and 1.72% of potassium hydroxide required for the saponification of the acetylated oils. The results are somwhat low, owing to the dehydrating action of the acetic anhydride used in the acetylation.

Cedar-wood oil is largely used as an adulterant of sandalwood oil. It may be detected and estimated as described on page 129. It has also been found as an adulterant of peppermint oil, orris oil, lemon oil, lavender oil, geranium oil, chamomile oil, cassia oil and anise oil. In addition to its employment with oil-immersion lenses, it is used in soap perfumery, in leather manufacture, in wood polishes etc.

Adulteration of this oil is not very frequent. Pure oil may be known by its sp. gr., high lævorotatory power, and the saponification values before and after acetylation.

The following table gives the chief characters of the less important oils of commerce (chiefly from Schimmel's reports).

| Source | Sp. gr. 15° | Opt. rot. | Ref. ind. | Solubility, 90 % alc. | Character and constituents |
|---|---|---|---|---|---|
| Cedrus atlantica.... | 0.950 to 0.968 | +46° to +62° | 1.5120 to 1.517 | 1 in 10 vols. | Light brown color. Balsamic odor. Acetone; d-cadinene. |
| Hayti........... . | 0.9612 | −15° | ........ | 10 vols. incomplete | Lemon yellow color. Balsamic odor. |
| Cedrus libani....... | 0.940 to 0.947 | +68° to +86° | 1.5125 to 1.5134 | 1 in 5 to 6 vols. | Lemon yellow color. Balsamic odor. |
| Cedrus deodara..... | 0.9549 to 0.9756 | +52 25° to +54.1° | 1.5195 to 1.5225 | ........... | Reddish color. Balsamic odor. Ketone; phenol; sesquiterpenes. |

In addition to the above several oils erroneously designated "cedarwood oils" have been distilled from cedrela sp. in various parts of the world.

## Cedar-leaf Oil

This oil should, presumably, be obtained by the distillation of the leaves of the red cedar, *Juniperus virginiana*, but other leaves, such as of *Thuja occidentalis*, are used in its preparation. Many conifers in North America pass under the name of "cedar;" thus *Thuja occidentalis*, and *Chamæcyparis sphæroidea* are termed "white cedar."

The true cedar-leaf oil, from *J. virginiana*, is rarely found on the market. It is an oil having a pleasant, sweetish odour. Gildemeister and Hoffmann (*The Volatile Oils*) state that this oil has a sp. gr. of 0.887 to 0.900, and an opt. rot. of +59.40°. It is insoluble in 10 parts of 80% alcohol. A large portion of the oil distils below 180°, of which the greater part comes over between 173° and 176°. This fraction consists of dextrolimonene. Other terpenes are also present, including α-pinene. Cadinene is contained in the higher fractions, while borneol and bornyl esters (including probably bornyl valerate) are also present in the oil.

The following analyses of commercial oils showing the differences existing between them and pure oil of cedar-leaf are given by Schimmel & Co. (*Rep.* April, 1898, 14):

|  | Sp. gr. | Opt. rot. | Sol. in 70% alcohol |
|---|---|---|---|
| Pure | 0.887 | $+59.4°$ | Very insoluble |
|  | 0.897 | $-12.4°$ | Insoluble |
|  | 0.886 | $- 3.7°$ | Insoluble |
|  | 0.887 | $-24.2°$ | Insoluble |
|  | 0.920 | $-10.4°$ | 1 in 4 |
|  | 0.918 | $-11°$ | 1 in 5 |
|  | 0.905 | $-10°$ . | Insoluble |

All these samples contained more or less oil of thuja, as was evident from their odour.

Commercial oil of cedar-leaf is thus usually obtained by the distillation of miscellaneous conifer-needles, including those of thuja. Red thuja oil is sometimes met with under the name "cedar oil." The true cedar-leaf oil is much more valuable than either cedar-wood oil or the oils from thuja and other varieties of conifers.

**Celery Oil.**—All parts of the herb *Apium graveolens*, the common celery, yield an essential oil, of which that from the seeds is most valued. Schimmel & Co., state that that from the green leaves most exactly reproduces the natural celery flavour. The oil from the seed is obtained to the extent of about 3%, as a liquid of strong celery odour, having a sp. gr. 0.870 to 0.895 and an opt. rot. $+60°$ to $+82°$, ref. ind. at 20° 1.478 to 1.486. The chief constituent of the oil is dextrolimonene. Ciamician and Silber (*Ber.*, 1897, **30,** 492) examined the high boiling fractions of the oil and found traces of palmitic acid, guaiacol and a crystalline substance of the formula $C_{16}H_{20}O_3$, m. p. 66° to 67°. In addition, a sesquiterpene was found, and 2 bodies, both acids, of a peculiar constitution, *sedanolic* and *sedanonic acids*, together with the lactone of the former, *sedanolide*, which appears to be the chief odoriferus constituent of the oil. *Sedanolic acid*, $C_{12}H_{20}O_3$, a crystalline substance, m. p. 88° to 89°, is easily converted into its lactone, sedanolide $C_{12}H_{18}O_2$. *Sedanonic acid*, $C_{12}H_{18}O_3$, melts at 113°, and possibly occurs as an anhydride in the oil. These 2 acids are closely related, and Ciamician and Silber consider that sedanolic acid is *o*-oxyamyl-tetrahydrobenzoic acid, and that sedanonic acid is a related ketonic acid.

Schimmel & Co. (*Report*, April, 1910, 32) isolated and described the sesquiterpene present in this oil, which they prepared by regenerating the hydrocarbon from its crude hydrochloride. Its charac-

ters were given as follows: b. p. 268–272°, sp. gr. 0.9196 at 20°, opt. rot. +49° 30′ and ref. index 1.5048. Semmler and Risse (*Ber.*, 1912, **45,** 3301) consider that a second sesquiterpene has been present, and that, after the elimination of this, pure selinene should have a rotation of +61° 36′ and a ref. index 1.5092.

Schimmel & Co. (*Rep.*, 1909, 37) give the following data for an oil distilled from a wild celery in the south of France. It was pale yellow and of a pronounced celery odour. No clear solution could be obtained even with 95% alcohol, due to the fact that the sample was about a year old and had become much resinified. By distillation with steam (leaving 7.7% residuum) the constants were: sp. gr. 15° 0.8541; opt. rot. +71°; ind. ref. 1.47489. This rectified sample was soluble in 6 volumes and more of 90% alcohol.

An Algerian oil distilled from wild plants had the following characters; sp. gr. 0.8467; opt. rot. +69.3°.

Green celery herb yields 0.1% oil with the following characters; sp. gr. 0.848 to 0.880; opt. rot. +41° to +60°; ref. ind. 1.478 to 1.481; soluble in 10 vols. of 90% alcohol.

Oil of celery is used in flavouring condiments and sauces.

## Chamomile Oils

Chamomile oil occurs in commerce in 2 varieties, namely, Roman chamomile oil and German chamomile oil. The former is the oil distilled from the flowers of *Anthemis nobilis;* the latter is obtained from the flowers of *Matricaria chamomilla.*

**Roman chamomile oil** is a pale blue or greenish-blue oil when freshly distilled, gradually becoming yellowish-brown. It has the aromatic taste and odour of the flowers. The sp. gr. of the oil ranges from 0.904 to 0.918 at 15°, and it is slightly optically active ($-3°$ to $+4°$), soluble in 6 to 10 vols. 70% alcohol, often turbid.

Roman chamomile oil is remarkable for the number of compounds of the aliphatic series which occur in it. These compounds include isobutyl isobutyrate and angelate; amyl tiglate and angelate; hexyl tiglate and angelate; and *anthemol,* $C_{10}H_{16}O$, as was shown by the researches of Demarcay. Naudin (*Bull. Soc. Chim.* [2], 1884, **41,** 483) also isolated a hydrocarbon of the olefine series, which contained $C_{18}H_{36}$ and was termed by him *anthemene.* It crystallises in needles, m. p. 63°.

According to Blaise (*Bull. Soc. Chim.* [3], 1903, **29,** 327), Roman chamomile oil does not contain any compound of tiglic acid, the small quantities usually found being due to the action of alkali on the angelic acid on saponification.   Angelic acid forms 80% of the total acids in the oil.

*Angelic* and *tiglic acids* are stereo-isomers, unsaturated acids of the acrylic series.

Angelic acid melts at 45°, while tiglic acid melts at 64.5° to 65°.

There are no recognised methods for the analysis of chamomile oil.   The properties, as described by the Pharmacopœia, should be noted.   This is characteristic, both in the case of Roman and German chamomile oils.   Doubtful samples should be submitted to a comparative test with a specimen of the pure oil.   The sp. gr. of the Roman chamomile oil should come within the limits specified above.

A. Jama (*Apoth. Ztg.*, 1909, **24,** 585) obtained oils from both calyx and the entire flower and found the following values:

Flower, sp. gr. 0.954., ind. ref. 1.3637, sap. value 74.4;

Calyx, sp. gr. 0.949, ind. ref. 1.3637, sap. value 33.7.

Neither oil had appreciable optical activity.

**Chrysanthemum oil,** distilled from the green leaves of *Chrysanthemum japonicum* (the autumn chrysanthenum), is considered by Perrier to resemble the oil of Roman chamomile.   The yield is about 0.16% of a green oil having an odour of peppermint and chamomile. Chrysanthemum oil begins to boil at 160°, and has a sp. gr. of 0.932 at 15° and a ref. index of 1.4931 at 18°.   It is soluble in 10 volumes of 95% alcohol, but is nearly insoluble in alcohol of 70%.   When cooled to a very low temperature, the oil solidifies.   It contains an aldehydic substance which combines with sodium hydrogen sulphite, and apparently it also contains angelic acid.

**German chamomile oil** is blue, the colour changing gradually by the influence of light to green, and finally brown.   Its sp. gr. at 15° is 0.920 to 0.955.   It was found by Kachler to contain an acid which has since been identified as *caprinic acid*.   Schimmel & Co. state that the average saponification value is 45; it is highly probable that it contains a notable quanitty of esters.

German chamomile oil, when cooled to a low temperature, becomes a semi-solid mass of the consistence of butter.   Schimmel & Co. (*Report*, April, 1894) have shown that this behaviour is due to the

presence of a paraffin or mixture of hydrocarbons. This paraffin dissolves with difficulty in alcohol; but it is readily soluble in ether, and persistently retains the blue of the oil. When quite pure, it is said to be a brilliant white substance, m. p. 53° to 54°, showing all the properties of a paraffin.

German chamomile oil of commerce is said to be sometimes adulterated with oil of milfoil and with cedar-wood oil. Oil of milfoil is a blue oil, but as its odour is quite different from that of chamomile oil, it would be impossible to add it in any quantity without detection. Chamomile oil adulterated with an appreciable quantity of cedarwood oil remains liquid at 0° (Schimmel & Co.), whereas the genuine oil begins to thicken at 15° and congeals at 1°. The oils of copaiba, lemon, and turpentine are also used as adulterants of chamomile oil.

## Champaca Oil

This oil, somewhat resembling ylang-ylang oil, is one of very high perfume value. It is distilled from the flowers of *Michelia champaca*, a plant cultivated, and also growing wild, in the forests of the Himalayas, from Nepal and Kumaon eastwards; and also in the Nilghiris and Travancore, Java and the Philippines. The flowers, which are of an exquisite odour, are not unlike a double narcissus. The essential oil distilled from the flowers is known in India as *Pand* or *Champa-ka-utter*. The oil is known as *Yellow Champaca*, whilst that from *Michelia longifolia* is known as *White Champaca*. A sample of the former distilled in Java (yellow champaca oil) was a pale yellow oil of thin consistence, resembling, in a degree, oil of orris in odour. It had a sp. gr. 0.914, and an opt. rot. − 13° 14′. The oil of white champaca from the same source had a sp. gr. 0.883 to 0.897, an opt. rot. −12° 50′ and ref. index 1.4470. Its odour recalled that of basil. According to Schimmel & Co., the sp. gr. of the oil from *Michelia champaca* varies from 0.907 to 0.940 and the opt. rot. from −12° 18′ to −55°.

According to Bacon (*Philippine J. Sci.*, 1910, **5**, 262) the oil deposits crystals, and on standing for a time becomes semi-solid. Brooks (*Phillipine J. Sci.* 1911, **6**, 333) states that the oil has a sp. gr. of 0.904 to 0.9107 at 30°/30°, ref. index 1.4640 to 1.4688, and ester value after acetylation 199. Benzyl alcohol and benzaldehyde are constituents of the oil.

The leaf oil which is prepared on a commercial scale in Java has a sp. gr. 0.922, opt. rot. +12° 30', ester value about 25, and ester value after acetylation about 60 to 65.

## Chenopodium Oil (American Wormseed Oil)

This oil is distilled from the nearly matured herb of *Chenopodium ambrosioides anthelminticum* L., the major portion of the oil being in the nearly ripe fruit. It is a light yellow oil of peculiar characteristic odour.

The U. S. P. (9th rev.) requires the official oil to be soluble in 8 vols. of 70% alcohol and to have an opt. rot. of −4° to −10°, and a sp. gr. of 0.955 to 0.980 at 25°.

Russell (*J. Am. Phar. Assn.* XI, 4, 255, 1922) examined oils personally collected at the still, and found that the sp. gr. is influenced by the method of distillation. With a rapid distillation oils possessing the U. S. P. requirements were obtained, whereas with a slow distillation oils were obtained whose sp. gr. did not meet the requirements of the U. S. P. The amount of ascaridole present in the oil was likewise influenced by the method of distillation.

E. K. Nelson (*J. Am. Chem. Soc.*, 1911, **33**, 1405; 1913, **35**, 84; 1920, **42**, 1204) has published an exhaustive investigation on the constitution of ascaridole, which is the active constituent of this oil. He has evolved a method (*J. Am. Phar. Assn.* 836, **10**, 1921) for the estimation of this constituent which is as follows; 10 c.c. of the oil are placed in a 100 c.c. cassia flask, and to this are added 75 c.c. of a 60% by volume solution of acetic acid (60 c.c. of glacial acetic acid are made to 100 c.c. with distilled water). The flask is then thoroughly shaken and the oil brought into the neck of the flask by the addition of more 60% acetic acid. After the undissolved oil is completely in the neck of the flask, which occurs after standing for some time and can be hastened by twirling the flask, its volume is read off and subtracted from ten, and this difference multiplied by ten expresses the per cent. by volume of ascaridole.

The constituents of chenopodium oil thus far isolated are ascaridole (an organic peroxide to which the anthelmintic properties of the oil are due and which is present to the extent of 60–70%), α-terpinene, *p*-cymene, and a new terpene (described by Henry and Paget) *J. Chem. Soc.* 1921, 709, 1714.

*d*-Camphor has been found in at least two samples in small amount. Its presence in the pure oils is doubtful.

Chenopodium oil is used medicinally as an anthelmintic, especially in the treatment of hookworm.

## Clove Oil

Clove oil is obtained by distillation from the buds and stems of *Eugenia caryophyllata*. A cheap and inferior oil is made from the stems of the clove-plant. It appears to contain no acetyl-eugenol.

Clove leaf oil closely resembles clove bud oil in characters, and contains from 78 to 88% of eugenol.

Clove oil has the characteristic odour of cloves, and a pungent taste. When freshly distilled, the oil is colourless or faintly yellow, but the colour deepens on keeping. The oil is also soluble in about 2 vols. of 70% alcohol. According to the U. S. P. (9th rev.) the sp. gr. varies from not less than 1.038 to 1.060 at 25°. Any sample with a lower sp. gr. than 1.030 is adulterated or suspicious. The opt. rot. of clove oil ranges from 0 to −1.2, and the b. p. should not be below 245°. The ref. ind. of the oil is an additional guide to its purity, the index being 1.530 to 1.535 at 20°.

E. J. Parry states that a sample of clove oil examined by him, which was an absolutely pure oil guaranteed by one of the most reputable drawers in England, had the low sp. gr. 1.0494 at 15.5°. It contained 84% of eugenol, estimated by Umney's potassium hydroxide absorption method, and answered to the B. P. tests in all other particulars. Parry suggests 1.048 as the minimum limit for the sp. gr. of the oil. Schimmel & Co. consider the limits of 1.043 to 1.068 at 15° to be compatible with genuine oils.

The chief and most important and abundant constituent of clove oil is the phenol, eugenol, $C_{10}H_{12}O_2$, the proportion ranging from 80 to 95%. The greater part of the eugenol is free, but there exist in clove oil esters of eugenol (chiefly acetate) in amount ranging from 7 to 17%. The sesquiterpene, caryophyllene, makes up the greater part of the remaining portion of the oil. Jorissen states that oil of cloves contains traces of a substance resembling or identical with vanillin, which possibly has its origin in the oxidation of eugenol. Heine & Co. state that traces of naphthalene are present in clove oil. Schimmel & Co. have found methyl alcohol, furfural,

and traces of an aldehyde (not acetaldehyde). They consider that the darkening of oil of cloves is probably partly due to the presence of furfural.

Schimmel & Co. (*Rep.*, April, 1897, 45) isolated from clove oil a very small quantity of a substance which appears to be normal amyl-methyl-ketone, $C_5H_{11}.CO.CH_3$. This is believed by them to be the other odoriferous constituent of the oil, as it imparts to a mixture of eugenol and caryophyllene a clove-like odour, even when added only in traces. Later, the discovery of methyl-heptyl-ketone and methyl benzoate in clove oil was announced by Schimmel & Co. (*Rep.*, 1902 and 1903, April).

Erdmann has observed the presence in clove oil of salicylic acid, probably combined as eugenol acetyl-salicylate. The same worker also confirmed Schimmel & Co.'s observations of the presence of furfural in the preliminary distillate of cloves.

From the highest boiling fractions of oil of clove stems (b. p. 143 to 155° at 9 mm.; $\alpha_D - 21^c$; $d^{20°}$ 0.966; $n_D^{20°}$ 1.5010) F. W. Semmler and E. W. Mayer (*Ber.*, 1912, 45, 1392) have isolated a sesquiterpene alcohol, $C_{15}H_{26}O$, which they found to possess the following constants: b. p. 138 to 148° (8 mm.), $d^{20°}$ 0.9681, $\alpha_D - 17°$, $n_D$ 1.5010, mol. refr. found 68.18, calc. for $C_{15}H_{26}O$, 68.07. Judging from these values, the substance is a bicyclic sesquiterpene alcohol with one double bond. The chloride of the alcohol (b. p. 147 to 155° at 12 mm.; $d^{20°}$ 0.990) when treated with alcoholic potash solution yields a hydrocarbon having the following properties: b. p. 123 to 126° (10 mm.), $d^{20°}$ 0.9273, $\alpha_D^{20°} - 23°$, $n_D^{20°}$ 1.5024.

S. T. Garde (*Perf.* and *Ess. Oil Record*, 115, 12, 1921) reports on clove stem oil distilled from Zanzibar stems; pale yellow colour, sp. gr. $\frac{34°}{37°}$ 1.054 to 1.0548; ref. ind. 1.5345; soluble in 0.5 vols. of 80% alcohol. Total eugenol by Umney's method 93.09%, by Thom's method 83.53%, free eugenol by Varley and Bolsing's method 69.86%.

The British Pharmacopœia (1914) states that oil of cloves should have a sp. gr. of 1.047 to 1.065, and that the alcoholic solution should turn blue with ferric chloride.

Unless the proportion of ferric chloride is very small, a bright green is produced. After shaking 1 pt. of the oil with 20 pts. of *hot* water, and filtering the aqueous liquid, the latter should not give a blue with

ferric chloride (absence of phenol), though a transient grey-green may be produced (U. S. P.).

Alcohol is occasionally added as an adulterant to oil of cloves. It lowers the characteristically high sp. gr. of the oil, and begins to distil over below 100°, whereas pure clove oil will yield no distillate below 245°.

Petroleum and oil of turpentine are sometimes used as adulterants of oil of cloves. Such sophistications can readily be detected by the decreased solubility of the oil in 90% alcohol.

The cheaper kinds of German clove oil are liable to partial abstraction of eugenol, or may be a mixture of pure oil with the residue (caryophyllene) from the manufacture of eugenol. Such oils have a low sp. gr., and are less soluble in 90% alcohol than pure oil of cloves. The eugenol content will be lessened.

An oil which was said to be used in certain German works as an adulterant of clove oil was found by Parry to consist of pure cedar-wood oil. Such an adulterant would lower the sp. gr. of the oil, whilst it would render it less soluble in 90% alcohol. It would also increase the lævorotation. Gurjun-balsam oil and camphor oil are said to have been used as adulterants.

Castor oil has recently been found as an adulterant of clove oil. This adulterant lowers the sp. gr. and the ref. index, and causes the oil, although soluble in 1.5 to 2 volumes of 70% alcohol, to become turbid on the addition of more alcohol.

The various methods for the estimation of eugenol in clove and other oils are described on page 501. According to E. C. Spurge (*Pharm. J.* [4], 1903, **16**, 701, 757), the estimation of the eugenol by Umney's method (uncorrected), together with the observation of the sp. gr., is sufficient for a pharmacopœia test. The U. S. P. (9th rev.) requires clove oil to contain at least 82% of eugenol when assayed by Umney's method (p. 501), 10 c.c. of the oil being employed with 100 c.c. of 5% potassium hydroxide solution, with which latter solution also the liquid is brought to the zero-mark in the flask.

Oil of cloves is used as a source of eugenol and caryophyllene; medicinally; and as a flavouring agent in confections, cordials and toothpastes. It is also used in perfumery, in the manufacture of vanillin, and in casein paints and porcelain enamels.

## Coriander Oil

Coriander oil is distilled from the fruit of *Coriandrum sativum*. It is a colourless or pale yellow oil, having an odour and flavour of the fruit.

The B. P. (1914) directs that the oil should have a sp. gr. of 0.870 to 0.885, ref. ind. 1.463 to 1.467; opt. rot. $+8$ to $+14$, and that 1 c.c. of the oil should yield a clear solution with 3 c.c. of 70% alcohol. The latter test shows the absence of oil of turpentine and added terpenes.

The U. S. P., (9th. rev.,) requires sp. gr. at 25° 0.863 to 0.875, solubility in 3 vols. of 70% alcohol, and opt. rot. $+8°$ to $+13°$.

The constituents of coriander oil have not been very thoroughly studied. The alcohol found by Semmler, and termed by him "coriandrol," has been proved by Barbier (*Compt. rend.*, 1893, **116**, 1459) to be dextrolinalol, $C_{10}H_{18}O$. This is the chief constituent. The substance to which oil of coriander owes its characteristic odour has not yet been isolated. Other constituents are pinene (three modifications), *p*-cymene, dipentene, terpinene, (two modifications), *n*-decylic aldehyde, geraniol, *l*-borneol, and the acetic esters of these alcohols. Possibly also phellandrene and terpinolene.

Oil of coriander differs in its composition according to whether it has been obtained from ripe or unripe fruits. The oil from the ripe fruit answers to the British and U. S. Pharmacopœia limits. Schimmel & Co. have investigated the nature of the oils distilled from the fruit, etc., at various periods of its growth. The results are shown in the following table:

| Nature of material | Sp. gr. at 15.5° | Rotation | Solubility in 70% alcohol | Remarks |
|---|---|---|---|---|
| 1. Oil from the entire flowering plant (green). | 0.853 | ......... | Insoluble | Objectionable odour which had almost entirely disappeared after $2\frac{1}{2}$ months. |
| Same, after keeping $2\frac{1}{2}$ months. | 0.856 | $+ 1.03°$ | ......... | ......... |
| 2. From green half-ripe herb with fruits. | 0.866 | $+ 7.2°$ | 1:3 | Odour of coriander with slight objectionable odour. |
| Same, after keeping 1 month.... | 0.869 | ......... | ......... | Pure coriander odour. |
| 3. From ripe coriander fruit....... | 0.876 | $+10.8°$ | 1:3 | ......... |

Schimmel & Co. (Rep., Oct., 1909, 47) found ref. ind. 1.4638 and ester value 20.22 in a sample distilled from ripe coriander seed. They consider that the linalool content should be 60 to 70%.

Parry (*Chemistry of Essential Oils*, 4th ed.) gives the sp. gr. of pure coriander oil as 0.870 to 0.885, the opt. rot. as $+7°$ to $+14°$, and the ref. index as 1.4635° to 1.4760. Sol. 3 vols. 70% alcohol.

The chief constituent of the oil being linalol, a large fraction (about 45 to 50%) should distil at 190° to 200°.

Orange oil, turpentine oil, and the oils of cedar-wood and cubeb have been used as adulterants of coriander oil. Orange and turpentine oils will be detected by the increase in the opt. rot., and also by the lowering of the sp. gr. The reverse effects will be produced by cedar and cubeb oils.

The oil is used in the manufacture of liquers, soaps and *eau de cologne.*

## Cubeb Oil

This oil is obtained by distilling the berry like fruit of *Piper cubeba.* Commercial cubebs are often adulterated with fruits of similar appearance. Thus J. Dekker (*Perf. and Ess. Oil Rec.*, 1913, **4,** 89) found in a sample of supposed cubebs four varieties of fruits, three of which were spurious. The oils from these varieties differed widely in their physical constants. As a means of distinguishing false fruits from true cubebs the sulphuric acid test is recommended. To the crushed berries in a porcelain dish add some conc. sulphuric acid. The genuine berries show a pink colour, the false berries a yellowish colour.

The oil is usually greenish or greenish-blue (occasionally greenish-yellow), and has the characteristic odour and flavour of cubebs.

The British Pharmacopœia (1914) states that the sp. gr. of the oil ranges from 0.910 to 0.930, but most samples of genuine oil of cubebs have a sp. gr. of 0.920 to 0.930. The rotation ranges between $-25$ and $-40°$.

The U. S. P., (9th. rev.,) states that the sp. gr. of the oil ranges from 0.905 to 0.925 at 25°, and that the opt. rot. should be $-20°$ to $-40°$ in a 100 mm. tube at 25°. The ref. ind. of oil of cubebs varies from 1.4935 to 1.4970.

The constituents of this oil have not as yet been thoroughly determined. One or more terpenes (including dipentene and probably pinene or camphene), and 2 sesquiterpenes (including cadinene) exist in the oil. Besides these, a sesquiterpene alcohol of the formula $C_{15}H_{25}OH$ is present, especially in the case of oils distilled from old

oxidised fruits. This substance is the so-called "*cubeb-camphor.*"
It crystallises in rhombic prisms melting at 65° to 67° (or, accord-
ing to Winckler, at 70°) and boils at 245° to 248°, with partial
decomposition.

The oil begins to boil at about 175° and distils mainly between
250° and 280°.

The following results were obtained on cubeb oils, recently distilled
by Messrs. Stafford Allen & Sons, Ltd.

| Sp. gr. at 25° C. | Rotation 100 m/m. | Ref. ind. at 25° | Distillate approx. % | |
|---|---|---|---|---|
| | | | Under 250° | 250°/280° |
| 0.919 | −29.4 | 1.4928 | 21.6 | 75.0 |
| 0.920 | −29.4 | 1.4930 | 29.0 | 66.0 |
| 0.923 | −29.1 | 1.4950 | 17.0 | 78.0 |
| 0.924 | −28.5 | 1.4944 | 32.0 | 64.0 |
| 0.923 | −27.2 | 1.4944 | 14.0 | 80.0 |
| 0.924 | −27.4 | 1.4949 | 22.0 | 72.0 |
| 0.927 | −27.2 | 1.4950 | 50.0 | 44.0 |

The higher fractions of the oil are blue, which has been erroneously
ascribed to the presence of copper. The cause is unknown.

Oil of cubebs is now rarely adulterated, owing to its low price.
The presence of turpentine oil would be revealed on fractionation.
Genuine oil of cubebs is soluble in 1 to 2.5 pts. of 90% alcohol.

Some spurious cubeb oil, distilled from a species of *Piper*, not yet
identified, has been found on the market. Umney and Potter
(*Chem. and Druggist*, 1912, **80**, 331, 443) found it to have an opt.
rot. of about −14°. Another sample examined by the same
investigators had sp. gr. 0.894, opt. rot. +16° and a noticeable
difference in boiling temperature when compared with authentic
oil.

C. T. Bennett (*Perf. Ess. Oil Rec.* 1921, **12**, 90) describes a cubeb
oil giving colour tests indicative of gurjun balsam oil, but having
all other characters, except colour, corresponding to the requirements
of the British Pharmacopœia. The abnormality was finally shown
to be due to the fact that the oil was distilled from small and imma-
ture but genuine fruits of cubeb.

A sample of false cubeb oil (Evans, *Ann. Rpt.*, 1913) had the follow-
ing characters: sp. gr. 0.916; opt. rot. −9.5°; ref. ind. 1.4921.

In the fractional distillation of the oil, a considerable amount should pass over between 250° and 280°. A sample having a sp. gr. 0.913, opt. rot. −24° and ref. index 1.4915 gave the following results on fractionation:

Below 175°................................................ Nil.
      180°................................................  4%
      185°................................................  7%
      190°................................................ 10%
      200°................................................ 14%
      210°................................................ 18%
      220°................................................ 22%
      230°................................................ 25%
      240°................................................ 28%
      250°................................................ 33%
Above 250°............................................... 67%

The oil is used medicinally.

## Cumin Oil or Cummin Oil.   (Roman Caraway Oil)

This oil is obtained by the distillation of the fruit from *Cuminum cyminum.* It is an almost colourless or light yellow oil, with a characteristic odour and bitterness.

The oil from the fruit has a sp. gr. of 0.900 to 0.930. The opt. rot. of these oils ranges from +3 to +8; ref. ind. 1.494 to 1.507.

Oil distilled from seed obtained in Cyprus had a sp. gr. 0.953 to 0.956; opt. rot. +1.5° to +1.7°; ref. ind. 1.510 to 1.514; aldehydes 47% to 52%. The oil generally contains from 30% to 40% of aldehydes.

Oil of cumin is soluble in 3 to 10 vols. of 80% alcohol. The solubility of the oil depends upon the amount of cuminic aldehyde present, oils of a high sp. gr. (containing much of this heavy constituent) being soluble in 3 parts of 80% alcohol, and lighter oils requiring as much as 10 parts of 80K alcohol.

The oil contains α-pinene, β-pinene, paracymene, dipentene, α-terpineol, β-phellandrene (?), cuminic aldehyde, hydrocuminic aldehyde and cuminic alcohol. Cuminic aldehyde may be isolated and estimated in the following way (Kraut, *Ann.*, 1854, **92,** 66): The terpenes of the oil are removed by distillation, only the portion boiling above 190° being reserved for further treatment. This high-boiling fraction is next shaken with sodium hydrogen sulphite solution, the resultant crystalline mass being pressed after standing

for 24 hours.    The crystals are then washed with a mixture of alcohol and ether, and distilled with a solution of sodium carbonate. The oil is used as a source of cuminic aldehyde.

## Cypress Leaf Oil

The oil from the leaves of *Cupressus sempervirens* has, during the past few years, become very popular as a remedy for whooping-cough.

The oil contains a mixture of terpenes, a ketone resembling thujone, a sesquiterpene, cedrol, sabinol, a sesquiterpene alcohol, and esters of terpineol.

The oil has the following characters:

|  | German distilled | French distilled | Algerian distilled |
|---|---|---|---|
| Sp. gr.................... | 0.880–0.900 | 0.868–0.884 | 0.8764 |
| Rotation................. | +4° to +18° | +12° to +31° | +22° 18′ |
| Ref. index............... | 1.4740–1.4800 | 1.4710–1.4760 | ............. |
| Acid value............... | 1.5 to 3.0 | 0 to 2 | ............. |
| Ester value.............. | 13 to 22 | 3 to 14 | ........ .... |
| Ester value after acetylation.. | 36 to 57 | 9 to 32 | ............. |

In 1916 Schimmel and Co. (*Report* Apr./Oct.) reported on a of oil of cypress evidently adulterated so that the constants resembled true cypress oil.    The odour of the oil resembled rosemary. In 1919 (*Report* Apr./Oct.) the same firm report on a sample of cypress oil so old as to be no longer of therapeutic value.

## Dill Oil

This oil is distilled from the fruit of *Anethum graveolens*.    It is pale yellow, with an odour of the fruit and a sweet, aromatic taste. The British Pharmacopœia (1914) requires it to have a sp. gr. of 0.900 to 0.915 at 15.5°.    It should have an opt. rot. of +70 to +80°; ref. ind 1.483 − 1.488 at 25°.    Soluble in 3 vols. 90% alcohol.

The constituents of the oil of dill comprise carvone 30–60%, dextrolimonene, phellandrene (stated by Schimmel & Co. to be present in English and Spanish oils), a paraffin hydrocarbon, and "dill-apiole" (in Indian dill oil, which is the product of *Anethum*

*sowa*). This substance is isomeric with "apiole," present in oil of parsley. Dill apiole and dill isoapiole are also found in Spanish oil.

Oil of dill thus resembles caraway oil in composition, but it contains less carvone than the latter oil. The odours of the 2 oils are quite different.

Oil of dill differs in character according to its origin. J. C. Umney (*Pharm. J.*, [4], 1898, **7**, 176) has pointed out the differences between the oil obtained from English fruits and that from India dill fruit. Indian oil of dill has a higher sp. gr. and a smaller carvone content than the English oil. The following results were obtained by Umney on 5 samples of oil of dill. The Japanese oil resembles Indian dill oil in its characters:

| Oil | Sp. gr. | Rotation | Fractional distillation, % | | | | |
|---|---|---|---|---|---|---|---|
| | | | Below 200° | 200–210° | 210–220° | 220–230° | Above 230° |
| English...... | 0.9148 | +72.25° | 22 | 14 | 12 | 50 | 2 |
| English...... | 0.9146 | +80.25° | 21 | 19 | 12 | 46 | 2 |
| German..... | 0.9002 | +70.25° | 53 | 13 | 12 | 17 | 5 |
| Indian...... | 0.9486 | +47.5° | 24 | 17.5 | 7 | 10.5 | 39 |
| Japanese.... | 0.9643 | +50.5° | 21 | 12 | 10 | 8 | 49 |

German dill oil is similar to English dill oil, but Umney considered that the above sample of German dill oil had suffered partial deprivation of its carvone. Schimmel & Co. state that although the sp. gr. of this sample is somewhat low, yet it is quite consistent with a pure oil. They record 8 examples of oils of Thuringian dill with sp. gr. ranging from 0.899 to 0.911.

The German dill oil is distilled from ripe fruits, whereas the English dill oil is distilled from slightly immature fruits, which may account for the difference in constants.

The physical constants of dill oil are the most trustworthy by which to judge of the quality of a sample. The sp. gr. of European oils should lie between 0.900 and 0.918, and the opt. rot. should be from +70 to +82°. These figures should be taken as maximum and minimum limits. Fractional distillation is valuable as a method for the approximate estimation of carvone. Not more than 15 to 20% of the oil should distil below 185°, and at least 35 to 40% between 185° and 225°. Parry states that not less than 40% should distil above 220°. The ref. index is about 1.4900.

In order to exclude the apiole-containing oil from Asiatic fruits, the official characters of the oil (*Oleum anethi*) should be adhered to (Umney).

Dill-apiole, like its isomer apiole, is converted by the action of alcoholic potassium hydroxide into an isomeric product, by an alteration of the allyl- to the propenyl-group. Dill-apiole is a thick, oily liquid, with a b. p. of 285°. Iso-dill-apiole, formed by the action of alcoholic potassium hydroxide, is a substance forming colourless prisms melting at 44°, and boiling with slight decomposition at 296°. Bromine forms a tribromo-derivative with both apiole and dill-apiole.

Dill oil is used medicinally.

### Eucalyptus Oils

The oils distilled from the leaves of species of *Eucalyptus* differ so much in their physical characters and chemical composition that no sufficient indication is afforded of the nature of the oil unless the species of eucalyptus is stated.

The constituents of these oils include dextro- and lævopinenes (the former of which was at first termed "eucalyptene"); phellandrene; probably camphene and fenchene; the sesquiterpene aromadendrene; cineole (eucalyptole); citronellal; citral; cuminal (?); citronellol; geraniol; geranyl acetate, and various aldehydes and esters; and the stearoptene eudesmol (p. 59). The oils used in medicine contain cineole as chief constituent. The official oil of the British Pharmacopœia (1914) is that from *E. globulus* and other species of eucalyptus, which usually contains at least 50 to 60% of cineole, and frequently up to 80%, together with pinene and traces of ethyl alcohol, amyl alcohol, and butyric, caproic, and valeric aldehydes.

According to H. G. Smith, the aldehyde occurring in a large number of eucalyptus oils is not cuminic aldehyde, as hitherto supposed, but a new aldehyde to which he gives the name *aromadendral* (p. 59).

The official oil (from *E. globulus*) is the most valued in medicine. The oils from *E. cneorifolia, E. dumosa, E. leucoxylon, E. oleosa, E. punctata* and *E. Morrisii* resemble that from *E. globulus* very closely in physical characters and chemical composition, and therefore frequently comply with the requirements of the British Pharma-

copœia. An oil answering to these requirements is colourless or pale yellow, having an aromatic camphoraceous odour and a pungent taste, leaving a sensation of coldness in the mouth. Sp. gr. 0.910 to 0.930. It should not rotate the plane of a ray of polarised light more than 10° in either direction, and it should contain not less than 55% by volume of cineole. If to 2 c.c. of the oil there are added 2 c.c. of glacial acetic acid, 4 c.c. of petroleum spirit and 3 c.c. of a saturated aqueous solution of sodium nitrite, the mixture, when gently stirred, should not form a crystalline mass (exclusion of eucalyptus oils containing much phellandrene). This last-named test is included in the United States Pharmacopœia (10th rev.).

The sp. gr. of the oils of eucalyptus range from 0.8596 to 0.9599 at 15°. The lower figure is only reached in the case of the oil from the leaves of *E. delegatensis*, which is largely composed of phellandrene, with very little cineole. The other oils range in sp. gr. from 0.870 to 0.960. Oils rich in phellandrene have a low sp. gr., whilst those having a high cineole-content approach the higher limit. The sp. gr. of pure cineole is 0.930 at 15°.

It has been pointed out by W. J. Brownscombe that eucalyptus oils other than *E. globulus* often answer the British Pharmacopœia tests, whilst some globulus oils do not respond to all the official requirements. Amongst the oils which have a fairly high cineole content, and yet do not exactly conform to the tests of the Pharmacopœia, are those from *E. eugenoides*, *E. macrorrhyncha*, and *E. odorata*. The last-named contains a notable amount of phellandrene.

Some authorities have suggested that the minimum sp. gr. of the British Pharmacopœia oil might preferably be fixed at 0.905. Oils having a cineole content of 45 to 52% and answering to the pharmacopœial requirements in every other respect, have been found to have sp. gr. ranging from 0.906 to 0.910 at 15°. Allen examined pure samples ranging from 0.907 to 0.930. The British Pharmacopœia limits are preferable, as they tend to keep up the cineole content.

It is not to be assumed, however, that any eucalyptus oil of sp. gr. near 0.930 is necessarily composed mainly of cineole. The researches of Baker and Smith (*J. & Proc. Roy Soc., N. S. Wales*, 1898, **32**, 104, 195) have shown that eudesmol and other high-boiling constituents of the oil of certain species of eucalyptus have high sp. gr. Thus an

oil containing a large proportion of eudesmol and a small amount of cineole will have a high sp. gr.

The rotation of the oils of eucalyptus is as irregular as the sp. gr. This is only to be expected, since some oils contain much of the inactive cineole, whilst others consist mainly of phellandrene, which has a very high optical rotation. The official oil is limited in its optical rotation from $+10$ to $-10$. Oils between these limits of optical activity and of the correct sp. gr. will contain a proper percentage of cineole. The optical rotation is not of much value. The U. S. Pharmacopœia (9th rev.) does not specify the optical rotation.

The most convenient test for the presence of phellandrene is based on the formation of *phellandrene nitrite*, $C_{10}H_{16}N_2O_3$. If much phellandrene is present, a crystalline mass of this compound will be produced when the oil is mixed with glacial acetic acid and sodium nitrite solution. A sample of eucalyptus oil purchased under the Sale of Food and Drugs Acts, and examined by A. R. Tankard in Allen's laboratory, had a sp. gr. of 0.8897, contained little or no cineole, but much phellandrene. It had a ref. index of 1.4830 at $25°$.

It has been shown by H. G. Smith (*Chemist and Druggist*, 1899, **54,** 534) that some eucalyptus oils are dextrorotatory when they contain the maximum amount of cineole, and that they do not then contain phellandrene, though this constituent may be present at certain times of the year.

According to Baker and Smith (*Chemist and Druggist*, 1899, **54,** 299) the emerald-green given by eucalyptus oils with the pharmacopœial nitrite test is not due to phellandrene, but to the pinenes present. Oils in which dextropinene is predominant are stated to give the colour to a more marked degree than those which contain an excess of lævopinene. Turpentine oil gives a brilliant green. A pure sample of *E. globulus* examined by Baker and Smith gave only a dull green with the nitrite test. The oil from *E. microcorys*, which consists very largely of dextropinene with some cineole, but contains no phellandrene, is stated by Baker and Smith to give a marked green. It is worthy of notice that an oil containing no cineole may give a more pronounced green than a pure oil.

**Estimation of Cineole.**—The phellandrene test and the estimation of the percentage of cineole are the most useful data on which to judge the quality of oils of eucalyptus. Several methods of estimat-

ing cineole have been based on its reaction with phosphoric acid. It was first pointed out by Scammel (Brit. Patent, 1894, 14138) that by the addition of concentrated phosphoric acid (sp. gr. 1.75 to 1.785, preferably the latter) in slight excess to the cineole-containing oil at a temperature not exceeding 60° F., the whole of the cineole is thrown down in the form of the crystalline phosphate. The cineole phosphate may then be treated in several ways. Thus it may be thoroughly pressed between blotting-paper, and the cake of phosphate weighed; or it may be decomposed with water (cold), and the free cineole weighed (as recommended by Scammel, who, however, used *hot* water); or the solution of cineole phosphate in water may be titrated, and the cineole calculated from the phosphoric acid indicated, assuming that one molecule of phosphoric acid is equivalent to one molecule of cineole.

E. J. Parry (*Chemistry of Essential Oils*) states that in his opinion this process, when carefully worked, gives results accurate to 3% when the oil contains at least 30% of cineole. If the cineole content is lower than this, the oil must be previously fractionated. Faulding (*Chemist and Druggist*, 1895, **46**, 311) also states that the cineole is quantitatively separated by Scammel's process.

According to H. G. Smith (*Chem. News*, 1902, **85**, 3), the pink obtained with some eucalyptus oils in the phosphoric acid test is due to a sesquiterpene termed by him *aromadendrene*. This hydrocarbon occurs in large amounts in the oil from *E. hæmastoma*. Aromadendrene boils at 260° to 265°, and has a sp. gr. of 0.925 at 19°. When the vapour of bromine is allowed to fall on its solution in glacial acetic acid, aromadendrene gives a crimson colour, which quickly changes to violet and finally to a deep indigo-blue.

With regard to the weighing of the pressed cake of cineole phosphate, D. B. Dott (*Pharm. J.* [4], 1899, **8**, 57) states that, in order to ensure the absence of terpenes and uncombined acid from the phosphate, it is essential to press the mass repeatedly between folds of blotting-paper. This requires some time, and there is risk of the absorption of water by the hygroscopic compound, thus causing error. The second method of procedure, that of weighing the free cineole after the decomposition of the phosphate compound with cold water, is held by Dott to be liable to give a result in excess of the truth, since the free cineole often contains a considerable quantity of undecomposed phosphate in solution. On the other

hand, if *hot water* or sodium carbonate solution be used to decompose the phosphate, loss may result owing to solution of the free cineole.

Dott has pointed out that cineole is much more soluble in diluted phosphoric acid than in water.

The third method, namely, that of titrating the phosphoric acid combined with the cineole, is preferred by Dott to the weighing of the pressed compound or of the free cineole. Too great an excess of phosphoric acid must be avoided. This is best done by estimating approximately the amount of cineole present, and then making another estimation with only a slight excess of phosphoric acid. L. F. Kebler recommends the following procedure (*Amer. J. Pharm.*, 1898, **70,** 492): 8 grm. (or less) of the oil in a beaker is cooled in ice-water, 4 c.c. of phosphoric acid solution (sp. gr. 1.75) added, and the mixture again placed in ice-water. When cool, the contents of the beaker are slowly and thoroughly mixed with a glass rod, the cineole phosphate separated, pressed, weighed, and decomposed with hot water. The acid is then titrated with a standard potassium hydroxide solution. According to the cineole content of the oil, it is occasionally necessary to add more than the specified quantity of phosphoric acid. Kebler obtained, by working on pure cineole, a result showing 103.75%. Fair approximations to the truth are thus obtained, the process being easy and rapid. Dott thinks it probable that, as water decomposes the phosphate compound, better results would be obtainable if anhydrous phosphoric acid were used.

W. H. Allen (*Chem. and Drug.*, 1899, **54,** 641) employs *warm* water for the decomposition of the phosphate compound, and finally washes the liberated cineole with warm water to remove any adhering traces of phosphoric acid.

The following process was described by Schimmel & Co. in their *Report*, 1909, **48**: 10 c.c. of the oil containing cineole are mixed in a cassia flask of 100 c.c. capacity with so much 50% resorcinol solution that the flask is filled for about $\frac{4}{5}$. The mixture is shaken thoroughly for 5 minutes, and the oil portions which have not entered into reaction are brought into the neck of the flask by adding resorcinol solution, and their volume determined. By subtracting this volume from 10 the cineole content of the oil is obtained, which is then expressed in % by volume by multiplication by 10.

The resorcinol method, advocated by Schimmel & Co., has not met with universal approval (p. 483). In cases where the

oil is very rich in cineole, the contents of the flask set to a solid mass and no reading is possible. This is to some extent obviated by diluting the oil with an equal volume of petroleum, and making the necessary correction in reading the unabsorbed portion. There is also no doubt (Bennett, *Chem. and Druggist,* 1908, **1,** 55; *Perf. and Ess. Oil Record,* 1912, 269) that other oxygenated constituents than cineole are absorbed, and that the process is not very accurate.

Dodge (*J. Ind. Eng. Chem.,* 1912, **4,** 259) in a communication to the 8th Inter. Con. of Appl. Chem. has suggested another method for the estimation of cineole.

This is based upon the familiar fact that, in the cold, cineole remains practically unattacked by potassium permanganate, whereas the remaining constituents of the oils in question (eucalyptus oil and cajuput oil) are oxidised into soluble compounds. The process is carried out as follows: 10 c.c. of the oil are placed in a narrow-necked flask, cooled with ice-water, and shaken with a gradually-added 5 to 6% solution of potassium permanganate, until the latter is present in excess. The mixture is then left standing in ice-water for from 12 to 18 hours with occasional shaking, after which the manganese peroxide which has separated is brought into solution by carefully adding sulphurous acid (or sodium hydrogen sulphite + hydrochloric acid). The unattacked oil (eucalyptol) is brought into the neck of the flask, pipetted into a graduated tube, washed with a little alkali, and estimated volumetrically. Its sp. gr. should be 0.929 to 0.930 (15°); it should be inactive, and dissolve in 3 to 5 volumes of 60% alcohol at 25°.

Bennett (*Perf. and Ess. Oil Record,* 1912, 295) has carried out a series of estimations with the following results:

|  | Cineole by per-manganate process | Cineole by phosphoric acid process | Resorcinol process |
|---|---|---|---|
|  | % | % | % |
| Eucalyptole..................... | 98 | ............. | ............. |
| Oil of eucalyptus, B. P.......... | 84 | 70 | 89 |
| Oil of eucalyptus globulus........ | 80 | 68 | 65 |
| Oil of eucalyptus amygdalina..... | 78 | ............. | ............. |
| Oil of cajuput, good quality....... | 80 | 52 | 54 |
| Oil of cajuput, fractionated....... | 70 | 14 | 17 |

It is evident from these experiments that, although the process may give approximate results with eucalyptole itself and with eucalyptus oils of high cineole content, it is not to be relied upon for cajuput oils or for eucalyptus oils of the amygdalina type, since these oils evidently contain constituents which are not readily oxidised by cold solution of permanganate.

T. T. Cocking (*Pharm., Jour.*, 1920, 105, 81–3) proposed the "Cresineol" method for cineole estimation.    3 grm. of eucalyptus oil, previously dried over CaCl₂, are mixed with 2.1 grm. of *o*-cresol and the freezing point of the mixture determined.    From a table prepared by Cocking the cineol content can be read direct.    When, however, the cineole falls below 45% (*Perf. and Ess. Oil Record*, 1921, 12, 339), a slight modification is recommended.    The sample under investigation is enriched with an equal weight of pure cineole and determination made of the freezing point.    A better course, however, is to use an equivalent amount of pure cresineol.    Thus after adding 2.1 grm. of *o*-cresol to 3 grm. of oil the mixture fails to crystallise at 24°, 5.1 grm. of pure cresineol are then added, the mixture gently warmed until liquid, then stirred, and the freezing point determined as described.

C. Kleber and W. von Rechenberg (*Jour. prakt. Chem.*, 1920, 101, 173) estimate cineole content of oil by means of the congealing point.    In a double-walled vessel (2 test tubes of varying diameters may constitute the vessel) place from 5 to 10 c.c. of oil and supercool in an ice and salt mixture, then bring the mass to solidification by rubbing the side of the tubes or by introducing a minute crystal of cineole.    Remove from cooling mixture and stir with thermometer until temperature ceases to rise.    This temperature is not, however the true freezing point, that being the temperature at which the crystallisation just begins or disappears. Hence the oil is made to melt and then only moderately cooled. After a few trials the solidification point can be noted to within tenths of a degree.    Oils containing less than 65% cineole are difficult of estimation, and in such cases the sample is mixed with an equal amount of cineole and the estimation made as indicated. The following table gives the cineole content of oils having congealing points from +1.2° to −19.6°.    Pure cineole congeals at +1.2°.

| Congealing temp. ° | Cineole % | Congealing temp. ° | Cineole % | Congealing temp. ° | Cineole % |
|---|---|---|---|---|---|
| +1.2 | 100 | −5.3 | 87 | −12.8 | 74 |
| +0.8 | 99 | −5.8 | 86 | −13.5 | 73 |
| +0.3 | 98 | −6.4 | 85 | −14.1 | 72 |
| +0.2 | 97 | −6.9 | 84 | −14.8 | 71 |
| +0.7 | 96 | −7.4 | 83 | −15.4 | 70 |
| −1.2 | 95 | −8.0 | 82 | −16.1 | 69 |
| −1.7 | 94 | −8.6 | 81 | −16.7 | 68 |
| −2.2 | 93 | −9.2 | 80 | −17.4 | 67 |
| −2.7 | 92 | −9.7 | 79 | −18.2 | 66 |
| −3.3 | 91 | −10.3 | 78 | −18.9 | 65 |
| −3.8 | 90 | −10.6 | 77 | −19.6 | 64 |
| −4.3 | 89 | −11.5 | 76 | ...... | .. |
| −4.8 | 88 | −12.2 | 75 | ...... | .. |

Eucalyptus oil has suffered adulteration by abstraction of its active constituent, cineole, and C. T. Bennett has recorded an instance of the wholesale sophistication of eucalyptus oil with 20% of castor oil (*Chemist and Drug.*, 1905, **67,** 33). The samples had a somewhat low cineole content, and left a considerable amount of viscous residue on distillation. This residue required a large proportion of potassium hydroxide for saponification, and glycerol was present in the liquid. Castor oil was detected by the usual tests. The presence of this adulterant is likely to be overlooked unless special tests are applied.

The oil from *Backhousia citriodora* consists almost entirely of citral (93 to 95%). The oil does not appear to be on the market.

Baker and Smith (*A Research on the Eucalypts and their Essential Oils*, 2nd Ed., 1921) describe the oils from 178 species of Eucalyptus. The reader is referred to the original work for detailed information on any species.

The following constituents have been found in Eucalyptus oils; cineole, geraniol, terpineol, piperitol, globuol, pinocarveol, eudesmol, aromadendral, cryptal, phellandral (?), citral, citronellal, butal-aldehyde, valeraldehyde, benzaldehyde, piperitone, tasmanol, aus-tralol, acetic and formic acids (free), geranyl-acetate, butyl-butyrate, amyl-eudesmate, amyl-phenylacetate (?), valeric acid ester, terpinyl-acetate, terpinyl-butyrate, pinene, phellandrene, limonene, dipen-tene, terpinene, aromadendrene, cymene and paraffin.

Eucalyptus oils are used as follows: *E. globulus*, *E. polybracta*, *E. smithii*, *E. dumosa*, as a source of eucalyptole, medicinally as a disinfectant and antiseptic, in dentrifices and disinfectant paints and varnishes; *E. amygdalina*, source of phellandrene and flotation of ores; *E. citriodora*, source of citronellal, soap perfume; *E. dives*, source of piperitone; *E. macarthuri*, source of geranyl-acetate; *E. oleosa*, solvent for fossil resins; *E. elemi*, perfumes and soaps; *E. estreigan*, culinary preparations.

## Fennel Oil

This oil is distilled from the fruit of several varieties of *Fœniculum vulgare*, which is found all over Europe except in the north and northeast, being especially common on the Mediterranean littoral; it is also found in Asia Minor, Persia, India and Japan.    Two oils are recognised in commerce, the "sweet" and "bitter" oils, the former being more esteemed.    The sweet fennel is said to be *Fœniculum sativum*, but this is probably only a variety of the common wild fennel.    The great variability in the fruits of different districts makes it necessary to fix some limits for the physical characters of the oil, which, however, may be exceeded in individual cases. The terpenes, pinene, phellandrene, dipentene and limonene, have all been detected in fennel oils, and the ketone fenchone, and anethole.   All these compounds, however, may not occur in any given sample.   Upon the presence of anethole, the value of the oil chiefly depends and the solidifying point of the oil is therefore a fair criterion of its value, if the oil is pure.   A good oil will, according to Parry, contain as much as 60% of anethole.   The sp. gr. should not fall below 0.960 nor above 0.980, and the optical rotation should vary from $+6°$ to $+20°$.   The solidifying point (see *Oil of Aniseed*) should not fall below $+5°$.   If necessary, the crystalline stearoptene may be separated and examined, but as a rule added solid bodies will alter the other characters of the oil.   The above tests will guard against the abstraction of anethole, or the addition of the residue of oil from which this body has been abstracted.

The U. S. P. (9th. rev.) states that oil of fennel is distilled from ripe fruits of the cultivated varieties of *Fœniculum vulgare*.   It has a sp. gr. at 25° of 0.953 to 0.973; an opt. rot. of $+12$ to $+24°$ in a 100 mm. tube at 25°; and is soluble in 8 vols. of 80% alcohol and in 1 vol. of 90% alcohol, forming a solution neutral to litmus.

The solidifying point is taken as described under oil of anise, the congealing point falling not below 3°. The tube containing the oil must be cooled to o° before crystallisation is induced.

Gildemeister and Hoffmann (*The Volatile Oils*, *2nd. edition*) report as in the following table on various fennel oils.

| Source | Sp. gr. 15° | Opt. rot. | Ind. ref. | Congeal-ing point | Principal constituent |
|--------|-------------|-----------|-----------|-------------------|----------------------|
| Germany, Fœniculum vulgare... | 0 965 to 0.977 | +11° to +20° | 1.528 to 1.538 | 5° to 10° | Anethole |
| Fœniculum dulce (Roman fennel). | 0.976 to 0.980 | +5° to +16.5° | ....... | 10° to 14.5° | Anethole |
| Macedonian fennel.. .. .. ... | 0.970 to 0.980 | +5° to +12° | . . . . | 7° to 12° | Anethole (fenchone absent) |
| Wild bitter fennel..... ...... | 0.905 to 0.925 | +40° to +68° | .. . ... | ......... | Phellandrene |
| Indian fennel.......... .... | 0.968 to 0 973 | +21° | ...... | 18.2° | Fenchone, anethole |
| Japanese fennel............. .. | 0.968 to 0 976 | +10° to +16° | .. . | 9° | Fenchone, anethole |
| Persian fennel....... ........ | 0.976 to 0.977 | +7° to +14° | ....... | 11° | ................. |

Fennel oil has been distilled from *F. capillaceum*, but differs from the seed oil with, the exception of Javanese oil, which resembles fennel oil of commerce.

Fennel oil is used medicinally and as a source of anethole and fenchone.

## Ginger Oil

This oil is distilled from the rhizomes of *Zingiber officinale*, a native of tropical Asia, which is cultivated in the East and West Indies, Africa, and to a small extent in Australia.

The constituents of the oil are as follows: *d*-camphene, β-phellandrene, cineole, citral, borneol, geraniol (?), the sesquiterpene zingiberene, decylic aldehyde, methyl heptenone, nonaldehyde, linalol, chavicol, zingiberol (a sesquiterpene alcohol to which the characteristic mild odour of ginger oil is due). Ginger oil has the following characters:

Sp. gr.................................... 0.875 to 0.886
Optical rotation........................... −28° to −50°
Acid value................................ o to 2
Ester value............................... o to 15
Ester value after acetylation................. 33 to 42
Ref. index................................ 1.4795 to 1.4855

Ginger oil is very sparingly soluble in alcohol, requiring from 6 to 10 volumes of 95% alcohol to give even an opalescent solution. According to Thresh, the English distilled oil yields the following fractions on distillation:

|  | % |
|---|---|
| Below 150°.......................................... | 5 |
| 150°–200°.......................................... | 10 |
| 200°–240°.......................................... | 8 |
| 240°–265°.......................................... | 60 |
| 265°–300°.......................................... | 7 |
| Residue.......................................... | 10 |

These results yield but little information, however, as decompositon goes on to a slight extent during distillation at ordinary pressures.

Ginger oil is used medicinally and as a flavouring for confections, wines, cordials and areated waters.

### Geranium Oil.  (Rose Geranium Oil)

The true geranium oil is distilled from the fresh flowering herb of species of *Pelargonium*, chiefly varieties of *P. odoratissimum, capitatum,* and *roseum.*   Rose petals are not infrequently distilled with the geranium plant to obtain a finer product, so that a true geranium oil is somewhat difficult to procure.   The true oils should not be confused with the so-called Indian (Turkish) "geranium" oil (Palmarosa oil), a product of the leaves of *Andropogon (Cymbopogon) Schœnanthus* (see p. 7), which is largely used as an adulterant of rose otto.

Geranium oil is colourless, or slightly green or brownish, and of pleasant rose-like odour.   Its sp. gr. ranges from 0.888 to 0.906 at 15.5°, and its opt. rot. between the limits −6° to −16°.   The oil is soluble in 3 volumes of 70% alcohol, a factor which is very useful in detecting adulteration.

The following are now accepted as the characters of the various types of geranium oil.

| | Sp. gr. | Rotation | Ref. index temp. | Esters |
|---|---|---|---|---|
| Réunion oil.......... | 0.888–0.896 | −7° to −14° | 1.462–1.468 | 21–33% |
| African oil.......... | 0.892–0.904 | −6° to −12° | 1.465–1.472 | 15–30% |
| French oil.......... | 0.896–0.905 | −7° to −11° | 1.463–1.469 | 19–28% |
| Spanish oil.......... | 0.897–0.907 | −7° to −11° | 1.462–1.469 | 27–42% |
| Corsican oil.......... | 0.896–0.901 | −8° to −11° | 1.461–1.471 | 22–27% |
| German oil.......... | 0.906 | −16° | ............. | 28% |

By using the acetylation and formylation processes, the following results have been obtained by various observers, in regard to the percentage of total alcohols and of citronellol present in different types of geranium oil:

| Oil | Total alcohols | Citronellol | Observer |
|---|---|---|---|
| African. ..................... | 69–79% | 32–43% | Simmons |
| Réunion..................... | 69–73% | 41–51% | Simmons |
| Corsican..................... | 69.8% | 30.3% | Simmons |
| Trappe de Staouéli............ | 71.5% | 27.9% | Simmons |
| French....................... | 72.7% | 39.8% | Umney |
| Algerian..................... | 74.1% | 32.9% | Umney |
| Bourbon..................... | 73.0% | 44.3% | Umney |
| Corsican.................... | 73.7% | 45.9% | Umney |
| Asian....................... | 69–72% | 51–62% | Umney |

Geraniol is the chief constituent of geranium oil, which also contains citronellol. The 2 alcoholic constituents of the oil range in amount from 60 to 70% (free), and, in addition, 20 to 40% of their esters are present, chiefly tiglates. (Detailed information concerning the proportions of the alcoholic constituents, and their estimation and separation, will be found on pp. 457 to 460.) A considerable amount of free acid is sometimes present in geranium oils, while esters of caproic, and probably of acetic, butyric, and valeric acids also occur in small quantities. The Algerian oils contain a smaller proportion of esters than other varieties. In addition, geranium oil contains lævomenthone, and small amounts of pinene, phellandrene, amyl alcohol, linalol, and a paraffin melting at 63°. Réunion oil is also stated to contain a blue high-boiling fraction, and according to Flateau and Labbé oleic acid is present as the geranyl ester, while other geranium oils are said to contain an acid having the formula $C_{14}H_{28}O_2$.

Geranium oils are liable to adulteration with fatty oils, and with the oils of turpentine and cedar-wood. All such additions tend to decrease the solubility of the oil in 70% alcohol. Fatty oils would be further detected by the presence of a non-volatile residue. The paraffin naturally occurring in geranium oils will rise to the surface on the addition of alcohol, while fatty oils tend to fall to the bottom of the containing vessel. Geranium oil is largely adulterated with the so-called Indian geranium oil (p. 7), an addition which causes

a lowered ester value.  An adulteration with benzoic esters has been reported by Schimmel.  This raises the ester value and is difficult to detect.

Artificial esters are now a common adulterant of geranium oil. Details as to the detection of these are to be found on pages 603 to 612.

Parry (*Perf. and Ess. Oil Record*, 1911, 83) has detected ethyl oxalate as an adulterant of this oil.  He gives the following particulars in reference to this adulteration.

Ethyl oxalate is a colourless, somewhat aromatic oil of sp. gr. 1.079 at 20°, and b. p. 186°.  It appears as rather more than twice its weight of geranyl acetate, or still more of geranyl tiglate.

The oils in question had the following characters:

|   | SP. GR. AT 15° | REF. IND. AT 20° | APPARENT ESTER VALUE, % | ROTATION |
|---|---|---|---|---|
| 1. | 0.9197 | 1.4703 | 57.5 | −10° 40′ |
| 2. | 0.9093 | 1.4702 | 46.0 | −10° 35′ |
| 3. | 0.9225 | 1.4634 | 74.0 | −10° 45′ |

Within a few minutes of the commencement of saponification under a reflux condenser, a good crop of silky crystals appears in the flask, due to the formation of potassium oxalate, which crystallises out.  The saponification liquid, freed from alcohol, and filtered from the decomposed oil, contained oxalic acid which was identified by the usual tests.

In an exhaustive classification of the geranium species and their odours, the reader is referred to an elaborate article on the genus *pelargonium* by E. M. Holmes. (*Perf. and Ess. Oil Record*, 1913, 239.)

Geranium oil is largely used in perfumery and is known as "rose-geranium" owing to the common practice of adding rose petals to the plants before distillation.  It is also used as a source of geraniol and citronellal, and as a flavouring for confectionary.

## Hyssop Oil

Examinations of this oil have been made by Schimmel & Co., their latest publication of data being in *Rep.* (Oct., 1909, 69).  The oil contains B-pinene and *l*-pinocamphone, the latter not hitherto found in essential oils.  The analytical data found by Schimmel & Co. are given in above quoted *Report* in comparison with oils

examined by Jeancard and Satie (*Amer. Perfumer*, 1909, **4,** 84) as follows. The dates given with J. and S. figures are the years in which the distillates were made. Schimmel & Co. consider that their data were not obtained from oils from the same species of hyssop as that used by J. and S.

|  | S. & Co. | J. & S. | |
|---|---|---|---|
|  |  | (1903) | (1908) |
| Sp. gr. (15°) ................ ........ | 0.925 to 0.940 | 0.9252 | 0.9262 |
| Opt. rot.................... .. | −17° to −24° 18′ | +1° | −2° 6′ |
| Acid value.................... ... | up to 3.1 | 0.8 | 0.8 |
| Ester value......... .... .... .. | 1.4 to 11 | 9.2 | 11.9 |
| Ester value (after acetylation)....... | 37 to 45 | 70.0 | 51.1 |

## Hop Oil

This oil is distilled from the flowers of *Humulus lupulus*. It is an oil with a pronounced odour of hops, and contains the following constituents: myrcene, linalol, an acid which exists in the form of esters, and which is probably isononylic acid; geraniol, α-caryophyllene, and β-caryophyllene (the two last named appear to be the true constituents of the body named *humulene* by Chapman (*Trans.*, 1895, **67,** 54, 780). Genuine hop oil has the following characters:

| | |
|---|---|
| Sp. gr.................................. | 0.855 to 0.895 |
| Opt. rot................................ | −1° to +1° |
| Ref. index.............................. | 1.4850 to 1.4925 |
| Acid value.............................. | 0 to 10 |
| Ester value............................. | 15 to 40 |
| Ester value after acetylation............ | about 70 to 80. |

As an adulterant of hop oil Schimmel & Co. report oils of copaiba and gurjun balsam. Both can be detected without difficulty by the high optical rotation and the solubility.

Oil of hops is used principally as a flavour in the manufacture of beers.

## Juniper Oil

This oil is obtained by the distillation of the fruit of *Juniperus communis*. The B. P., 1914, describes the oil as being "distilled from the ripe fruit and rectified." It has been pointed out by

Schimmel & Co. (*Rep.*, Oct., 1898) that the oil distilled on a commercial scale is obtained from the *ripe* fruits, and that the oil from unripe fruits is in all essential qualities inferior to the normal oil from ripe fruits.

Oil of juniper is colourless or pale greenish-yellow, with a characteristic odour, and a warm, aromatic, bitter taste. The B. P. directs that oil of juniper should have a sp. gr. of 0.862 to 0.890, and be soluble, with slight turbidity, in 4 times its volume of 95% alcohol. The U. S. P. (9th rev.) describes the oil as being soluble in 4 vols. of alcohol, with not more than a slight cloudiness. The solubility of the oil in alcohol is a valuable aid in testing its purity, but this solubility decreases greatly with age, a fact which should be borne in mind.

The constituents of oil of juniper include α-pinene, cadinene, camphene, a terpene alcohol (the so-called juniper camphor), esters and terpinenol. Terpineol does not appear to be present.

The sp. gr. of juniper oil usually ranges from 0.867 to 0.875, and these limits include the majority of samples. The pharmacopœia limits are therefore wide enough to include all genuine oils, and any departure from these limits may be taken as fairly certain evidence of adulteration. Old oils become thick through slow resinification and acquire an acid reaction and a more or less rancid odour. The age of the berries from which the oil is distilled also influences the sp. gr. of the oil.

Its sp. gr. rises and its solubility decreases, so that old juniper oil will not fulfil the requirements of the various Pharmacopœias.

Juniper oil is lævorotatory to the extent of about −10°. It rarely exceeds this limit, and is usually much less active, ranging from very slightly lævorotatory to about −7°.

This oil is sometimes slightly dextrorotatory (Russian oil) and is also as highly lævorotatory as −19° (Hungarian oil). Parry gives the ref. index as ranging from 1.4740 to 1.4880. S. & Co. (*Rep.*, Oct., 1909, 72) report a sample with a saponification value of 7.2.

Juniper oil is largely used for the manufacture of "gin-essence" (artificial gin). The true spirit is obtained by the distillation of the fermented juniper-berries, but gin-essence is an article of commerce consisting almost entirely of a solution of juniper-berry oil in alcohol.

Oils from the berries of *Juniperus phœnica* and of *J. oxycedrus* have a lower sp. gr. than the ordinary oil of juniper (0.850 to 0.860).

Their opt. activity is similar to that of the ordinary oil of juniper-berries. The wood of *J. oxycedrus*, on destructive distillation, yields the oil known as *Cade Oil*.

Fractional distillation serves as a method for the approximate estimation of the pinene and cadinene in the oil. Parry states that, with a series of fractionating bulbs, from 25 to 35% of the genuine oil will distil between 155° and 160°, and from 10 to 20% between 270° and 280°.

In distilling juniper oil fractionally, the last 20% should have a ref. index of 1.4950 to 1.5120. Adulteration with much turpentine will cause this figure to be lowered.

The wood of *J. communis*, when distilled with steam, is said to yield a volatile oil, but it is not an article of commerce. Commercial juniper-wood oil is, according to Parry, either an oil obtained by distilling turpentine oil over the wood or more often a mixture of turpentine with the oil from the juniper-berry. Less frequently it is composed of the waste terpenes from the preparation of so-called terpeneless oil of juniper.

A number of prosecutions have been instituted in England under the Food and Drugs Acts for the sale of "juniper oil" consisting of juniper-wood oil, and for adulteration of the oil with turpentine oil.

## Lavender Oils

The true lavender oil is obtained by the distillation of the flowers of *Lavandula vera*. It is a pale yellow or colourless oil, with a fragrant odour of the flowers and a pungent bitter taste.

The B. P. (1914) directs that the oil should have a sp. gr. 0.883 to 0.900, opt. rot. − 3° to − 10°, and that it should dissolve in 4 volumes of 70% alcohol. It should contain from 7 to 11% of esters (English oil) or not less than 30% esters (Foreign oil), calculated as linalyl acetate.

The U. S. P. (9th rev.) states that lavender oil must have a sp. gr. 0.875 to 0.888 at 25° opt. rot. − 1 to − 10 in a 100 m.m. tube at 25°, soluble in 3 vols. of 70% alcohol.

The usual English method of distilling lavender oil consists in collecting the last runnings (4 to 8% of the total distillate) apart from the major portion, since toward the end of the distillation decomposition products come over, causing a deterioration in the odour of the oil. The first distillates, as was shown by J. C. Umney's experi-

ments, have a lower sp. gr. (down to 0.881 in recently distilled samples) than the last runnings, which contain a larger proportion of esters.

The 2 chief varieties of this oil are the English and the French. French oil of lavender contains linalol (Bertram and Walbaum, *J. Prakt Chem.*, 1892, **45,** 590), linalyl acetate (25 to 40%); traces of $\alpha$-pinene and limonene, caryophyllene, geraniol (probably as esters); cineole, nerol, a stearoptene, coumarin, coumaric acid, and *d*-borneol. English oil differs from the French oil mainly in its percentage of linalyl acetate (7 to 9 or 11% only), and in containing a fairly large proportion of cineole, which imparts a characteristic pungency to the oil.

M. Duyk (*J. Pharm. Chim.*, 1896, [6], **4,** 453) states that lavender oil contains, in addition to the compounds mentioned in the text, the acetic, butyric, and valeric esters of borneol. Bouchardat (*Bull. Soc. Chim,* [3], 1894, **11,** 147) found dextrocamphene in the oil. Schimmel & Co. (*Rep.*, April and October, 1903) have announced the discovery of ethyl-amyl ketone, $C_8H_{16}O$, furfural (in first fractions), iso-amyl alcohol and an isomeric alcohol, together with esters of the former, in French lavender oil.

The sp. gr. of both English and French lavender oils varies between 0.883 and 0.900, rarely falling to 0.882.

The sp. gr. of genuine lavender oils will sometimes fall to 0.880, but in such cases care should be exercised in judging all the other analytical figures of such an abnormal oil. Old oils will often be found with abnormally high sp. gr., so that the age of the oil must be taken into account.

The addition of alcohol or turpentine oil as an adulterant lowers the sp. gr., while admixture of spike-lavender or cedar-wood oil raises this constant. Schimmel & Co. have observed the adulteration of lavender oil with resin, the addition of which raises the sp. gr. of the oil.

"When the oil is shaken with water in a narrow graduated cylinder its volume should not be diminished (absence of alcohol)."—U. S. P. (9th rev.).

The opt. rot. ranges from about $-33°$ to $-10°$. Lavender oils frequently suffer adulteration with oil of spike-lavender, when the optical activity is decreased, since the latter is dextrorotatory, $+1°$ to $+5°$. American turpentine oil has a similar effect, while the

lævorotation is also increased by the addition of French turpentine or cedar-wood oil. The ref. ind., according to Parry, ranges between 1.4600 and 1.4660.

That the odour of lavender oil is dependent on more than one of its constituents is shown by the fact that the English oil, containing far less linalyl acetate than French oil, commands a higher price. Thus the estimation of the ester content of an oil is not sufficient to decide its quality, and, in the case of English oils at least, it is necessary to take into account the purity of the odour as well as the chemical constants of the samples. Schimmel & Co. contend that the value of the oil increases as the ester content rises. There can be no doubt that the odour of lavender oil, due partly to the linalyl acetate (which has a bergamot odour), is modified to a very appreciable extent by other constituents, probably as yet unknown. Parry is of opinion that no definite relation exists between the ester content and the perfume value of French oil of lavender.

The ester content is of value when comparing oils from the flowers grown in the same district. The method usually employed is described on p. 602. English oils usually contain from 7 to 10% (sometimes 12%) of esters (calculated as linalyl acetate), while French oils contain about 30 to 40% or more. The finest oils produced in the south of Europe are those distilled from plants grown at great elevations.

Improvements in the methods of distillation appear to be responsible for occasional increases in the ester values of French and the other foreign lavender oils. A sample distilled at Barrême (*Perf. and Ess. Oil Record*, 1913, 4, 134) was found to contain 55.7% of esters, which is confirmed by Schimmel & Co. (*Report, Oct.*, 1913) who have found as much as 56% for oil distilled in this district. Samples distilled in Dalmatia have also been found to contain from 43 to 57% (*Perf. and Ess. Oil Record*, 1913, 4, 153).

The amount of esters present in oil of lavender is lowered by adulteration with either turpentine or spike-lavender oil, neither of which contains any notable amount of esters. Thus, as pointed out by Parry, mixtures of French lavender oil and spike oil can be made, having the same ester content (about 10%) as English oil, but the optical rotation will be lowered and the sp. gr. raised, though not to a very great extent. Much lavender oil is now adulterated with spike oil and ethyl succinate (see p. 71).

Other less important varieties of lavender oil are described in the table on pp. 202 and 203.

The presence of much *cineole* in the oil may be taken as evidence of the presence of spike oil so far as French oil of lavender is concerned, but English oil of lavender contains naturally notable amounts of cineole.

Schimmel & Co. have called attention to the adulteration of lavender oil with ethyl succinate, evidently added to give a fictitious ester value to the oil. 2 samples adulterated with this substance had a high sp. gr. (0.900; 0.905), and a high ester value (47.5; 48.5%). These adulterated oils contained approximately 8% of ethyl succinate, which would require about the same amount of alkali for saponification as 18% of linalyl acetate. For the detection of such adulteration, Schimmel & Co. proceed as follows: About 2 grm. of the oil are saponified, and the portion insoluble in water washed out with ether, the aqueous residue neutralised with acid, and diluted up to 50 c.c.; 10 c.c. of cold saturated barium chloride solution are added, the liquid warmed on the water-bath for 2 hours, and then cooled. The formation of any crystalline precipitate is indicative of adulteration, since the barium salts of acetic and butyric acids (the normal organic acids of lavender oil) are soluble.

*Ethyl citrate* is sometimes used as an adulterant, also for the same purpose as ethyl succinate, *i. e.*, to raise the ester value. The following method, proposed by Schimmel & Co., is stated to be more reliable than the barium method for detecting sophistications by means of added esters:

10 grm. of the oil to be examined are saponified for 1 hour on the water-bath with alcoholic potassium hydroxide solution, the contents of the flask then placed in a porcelain dish and the bulk of the alcohol evaporated. After this the liquid is washed in a separating funnel with about 100 c.c. of water, the oily portions removed by extraction with ether, the aqueous solution returned to the porcelain dish, and the bulk evaporated on the water-bath. When the alkaline solution has cooled it is acidified with sulphuric acid and the organic acids thus liberated absorbed with ether. The ethereal solution is then evaporated in a dish, and the residue is heated for some time on the water-bath to remove volatile (acetic and butyric) acids, then cooled, and digested with ether. A fine crystalline residue remains in case of an adulterated oil, which

may be identified by m. p., etc. These esters may also be detected by the methods as described under "esters," page 603 *et seq*.

The following table (*Report, Apr.*, 1912) shows the influence of certain adulterants on lavender oil. Samples Nos. 1 and 2 are adulterated with terpinyl acetate. No. 3 was abnormal, but as shown by an examination of the oil after steam distillation, the abnormalities were due to resinification, rather than to adulteration. No. 4 was adulterated with glyceryl acetate, and No. 5 is a pure high ester oil which gave identical, or nearly identical results, when different quantities of potash were used for saponification.

| Lavender oil | No. 1 | 2 | 3 Original oil | 3 Dist. with steam | 4 Original oil | 4 Shaken once with 5% alc. | 5 — 15 c.c. N/2 potassium hydroxide | 5 — 10 c.c. N/2 potassium hydroxide |
|---|---|---|---|---|---|---|---|---|
| $d^{15}$ | 0.9007 | 0.8946 | 0.9072 | 0.8932 | 0.8992 | ...... | 0.8913 | ..... |
| $\alpha_D$ | $-3°\,55'$ | $-2°\,34'$ | $-5°\,14'$ | $-5°\,37'$ | $-4°\,32'$ | ...... | $-8°\,43'$ | ..... |
| Solub. in 70% alcohol | 2.5 vol. | 2.5 vol. | 1.9 vol. | 2.2 vol. | 2.5 vol. | ...... | 4.5 vol. | ..... |
| Acid value | 0.3 | 0.5 | 0.8 | ...... | 0.5 | ...... | 0.3 | 0.3 |
| Ester value after 1 h. sap. with 10 c.c. N/2 solution | 78.4 | 83.3 | 100.5 | 102.5 | 90.0 | 87.0 | 145.7 | 143.4 |
| Ester content (calc. for linalyl ac.) | 27.4% | 29.2% | 35.2% | 35.9% | 31.5% | 30.4% | 51% | 50.2% |
| Ester value after 2 h. sap. with 20 c.c. ½ N. solution | 82.7 | 87.6 | 104.2 | 104.6 | 91.9 | ...... | 146.0 | 146.0 |
| Ester value after 1 h. sap. with 10 c.c. ½ N. solution + 25 c.c. alc. | 69.7 | 77.0 | 99.0 | 100.6 | 91.1 | ...... | 144.1 | 132.9 |
| Difference | 13.0 | 10.6 | 5.2 | 4.0 | 0.8 | ...... | 1.9 | 13.1 |
| Sap. value | 78.7 | 83.8 | 101.3 | 102.5 | 90.5 | ...... | ..... | ..... |
| Acid value II | 75.7 | 83.7 | 96.7 | 100.6 | 90.6 | ...... | ..... | ..... |
| Difference | 3.0 | 0.1 | 4.6 | 1.9 | ...... | ...... | ..... | ..... |
| Terpinyl acet. content, about | 5% | 4% | doubtful | | not ascertainable | ...... | ...... | ..... |
| Esters of spar. vol. acids | not ascertainable | | | | not ascertainable | ...... | ...... | ..... |
| Glyceryl ester | not ascertainable | | | not asc. | present | ...... | ...... | ..... |

*Salicylic* and *benzoic* acids have also been added to lavender oil. There presence is easily detected by the determination of the acid-number. Pure oil of lavender is practically free from acidity.

## Spike-lavender Oil

This oil is obtained by the distillation of the flowering herb, *Lavandula spica*. It is a pale yellow oil, with an odour resembling at the same time lavender and rosemary oils.

True lavender oil contains a notable amount of esters; oil of spike lavender is practically free, but contains a considerable proportion of alcoholic constituents. The composition of spike oil, which has been worked out chiefly by Bouchardat (*Compt. rend.*, 1887, **104**, 551; 1888, **107**, 53), is as follows: Linalol, cineole (a larger amount than English lavender oil), dextropinene, dextrocamphene, camphor, borneol, terpineol, and geraniol. A sesquiterpene is also supposed to be present, and traces of esters of the various alcohols also occur in the oil. The alcoholic substances, ascertained by the acetylation process and calculated as linalol, usually constitute about 30 to 40% of the oil. The method for the estimation of the alcohols in essential oils is given on page 593. The results are not strictly accurate, on account of the ease with which the alcohols decompose, but valuable comparative results are obtainable.

The sp. gr. of French spike lavender oil ranges from 0.905 to nearly 0.920, but it rarely exceeds 0.915. Probably 0.918 should be taken as the maximum limit. Spanish spike lavender oil ranges from 0.904 to 0.922. Adulteration with turpentine oil lowers the sp. gr.

The optical rotation of French spike oil ranges from $-3°$ to $+4°$, rarely up to $+7°$ Oils exceeding a rotation of $+5°$ should be regarded with suspicion. Spanish spike oil ranges from $-4.75°$ to $+15.75$, $15.75°$ rarely above $+8°$. Parry gives the ref. index as 1.4660.

Schimmel & Co. have proposed to fractionate the oil and take the opt. rot. of the first 10% distilled. The first 10% of the distillate of French oil is dextrogyrate up to $+10.75°$, occasionally higher or lower than the original rotation, whereas the Spanish oil gives an optical rotation of the first 10% of distillate up to $+14°$, as a rule not above $+8°$. The French oil has a ref. ind. 1.464 to 1.468, the Spanish oil 1.465 to 1.4653.

All spike oils of undoubted purity are stated to give a distinct dextrorotatory fraction, but Parry and Bennett have shown that certain spike oils are not only lævorotatory, but may yield a lævorotatory first fraction on distillation. An estimation of the total alcohols is required in these cases to ensure absence of French turpentine oil. An appreciable amount of French turpentine oil will render the fraction lævorotatory. It is necessary, in carrying out this test, to use Ladenburg's flask of uniform size, and to distil the

fraction (5 c.c. from 50 c.c of the oil) at the rate of not more than one drop per second. The following results were obtained by Schimmel & Co. by the analysis of 4 samples of genuine spike oil:

| Number | Sp. gr. | Rotation | Solubility in 70% alcohol | Rotation of first 10% of distillate |
|--------|---------|----------|---------------------------|-------------------------------------|
| 1 | 0.916 | $+7°\ 7'$ | 1 in 3 | $+7°\ 11'$ |
| 2 | 0.915 | $+3'$ | 1 in 2 | $+5°\ 10'$ |
| 3 | 0.914 | $+5°$ | 1 in 2.5 | $+7°\ 11'$ |
| 4 | 0.918 | $+5°\ 30'$ | 1 in 2.5 | $+6°\ 7'$ |

Parry and Bennett lay stress on the importance of examining the fractions obtained by the distillation of spike oil. An adulterated oil examined by them gave a fraction at 230° to 240° consisting of safrol.

Spike oil is soluble in 3 volumes of 70% alcohol. In this form, however, the solubility of spike oil is not of much value as a test for adulteration, since it has been shown by Parry and Bennett (*Chem. and Drug.*, 1903, **63,** 1011) that 25% of certain cheap adulterants may be added to spike oil without altering the solubility in 70% alcohol or the physical characters of the oil. Parry and Bennett suggest, therefore, that the solubility test should be altered, since it has been found that pure spike oils are soluble in 6 vols. of 65% alcohol. An addition of 5 to 10% of the usual adulterants (common rosemary oil, turpentine oil, and safrole) disturbs this solubility. Parry (*Chemistry of Essential Oils* (4th ed.)) states that pure spike oil is soluble in 2 to 2.5 vols. of 70% alcohol or in 3 to 4 vols. of 65% alcohol.

Genuine spike oils yield practically no ester value. This figure, together with the sp. gr., opt. rot., rotation of the first 10% distilled, and determination of the free alcohols, are most valuable data for testing the purity of this oil.

For the tendency of true and spike lavender flowers to hybridise, see Birckenstock (*Schimmel's Report*, Oct., 1906). The hybrid plants are known as "spigouse" and "lavandin," and the oils therefrom are midway in characters between lavender and spike oils.

Two typical lavandin oils gave the following results on analysis:

|  | 1 | 2 |
|---|---|---|
| Sp. gr.............................. | 0.9027 | 0.8995 |
| Optical rotation.................... | −0° 43′ | −1° 35′ |
| Ester value........................ | 6.23 | 9.12% |
| Total alcohols..................... | 34.8 | 36.5% |

Commercial spike oils, especially Spanish oil, are almost bound to contain small quantities of labiate oils other than true spike oil, because it is quite impossible to separate the flowers which are to be found growing side by side with genuine *Lavendula spica*, so that a mixture of these with a small quantity of allied species is usually thrown into the still.    The following are several varieties of lavender which are occasionally distilled.

The oil from *Lavandula pedunculata* has a sp. gr. 0.939 and optical rotation −45°.    It contains nearly 40% of esters, in addition to cineole and possibly thujone.    The oil of *Lavandula stœchas* (the "holy rosemary" of the Spaniards) resembles rosemary rather than lavender in its odour.    Its sp. gr. is about 0.940.    The oil of *Lavandula dentata*, of sp. gr. 0.926, also resembles rosemary, with a marked camphoraceous odour.    Charabot (*Bull. Soc. Chim.* **17,** 378) records the examination of a sample of Spanish lavender oil, but does not state its source.    He found in it much free linalol, but only 3% of esters.    Borneol was also present.

## Lemon Oil

This oil is produced chiefly in Sicily, and is probably one of the most complex of the essential oils.    It is obtained by expression of the fresh peel of lemons.

Lemon oil contains $\alpha$-pinene, $\beta$-pinene, camphene, $\beta$-phellandrene, methylheptenone, gamma terpinene, $d$-liminene, octylic and nonylic aldehydes, citronellal, $\alpha$-terpineol, citral, linalyl and geranyl acetates, bisabolene, cadinene and citroptene.    P. Barbier and L. Bouveault (also Burgess and Child) deny the occurrence of citronellal in oil of lemon.    Parry believes the methyl ester of anthranilic acid also to be present.

Limonene is the constituent of lemon oil which occurs in the greatest proportion, and is certainly responsible for some of the flavour

and odour of the oil. The compound to which the odour and strength of the oil is chiefly due, however, is citral. While citral is responsible for the primary odour of lemon oil, the esters geranyl acetate (in Messina and Palermo oils) and linalyl acetate (in Palermo oils), together with small amounts of octyl and nonyl aldehydes and other substances, modify it to such an extent that the purest citral obtainable is but a poor substitute for lemon flavour.

The characters of citral and of citronellal, and the methods for their estimation, are described on page 515 *et seq.* There has been much controversy as to the normal amount of citral (or rather, of total aldehydes) present in genuine oil of lemon, a standard of 7% being, until recently, insisted on.

A standard of not less than 4% citral has been adopted in the U. S. P., the oil being assayed by a given method. Lemon oil containing an addition of lemon-grass oil or lemon-grass citral would of course give a higher aldehyde content.

The method, as directed by the U. S. P. (9th. rev.) is as follows: Introduce about 15 c.c. oil of lemon into a 300 c.c. flask and note the exact weight; add 10 c.c. of an alcoholic solution of phenylhydrazine, (1 in 10) (not darker in colour than pale yellow), and allow it to stand for one half hour at room temperature. Then add a few drops of Methyl Orange T. S. and neutralise the liquid exactly by the cautious addition of $N/2$ HCl. If difficulty is experienced in detecting the end point of the reaction, continue the titration until the solution is distinctly acid, transfer the liquid to a separatory funnel and draw off the alcoholic portion. Now wash the oil with distilled water, adding the washings to the alcoholic solution, and titrate the latter with $N/2$ KOH.

Carry out a blank test identical with the foregoing, except that the oil of lemon is omitted, and note the amount of $N/2$ HCl consumed.

Subtract the number of c.c. of $N/2$ KOH from the number of c.c. of $N/2$ HCl consumed in the original test, and this result from the corresponding number of c.c. required in the blank test; each c.c. of this difference corresponds to 0.076 grm. of aldehydes, calculated as citral. It shows, when calculated from the weight of oil taken, not less than 4% of aldehydes from oil of lemon, calculated as citral.

Umney and Swinton (*Pharm. J.*, [4], 1898, **7,** 196) have found geranyl acetate to be present in lemon oil to the extent of 1.2 to 1.4%. This is true both of the Messina and Palermo varieties of

the oil, but in the latter a small quantity of linalyl acetate is also present.

Lemon oil has probably suffered more from adulteration than any other essential oil. The adulterants include turpentine oil, lemon and orange terpenes, distilled orange and lemon oils, lemon-grass oil, lemon-grass citral, cedar-wood oil, alcohol, stearin, castor oil and mixtures of alcohol and glyceryl acetate.

The British Pharmacopœia states that lemon oil should have a sp. gr. of 0.857 to 0.860, and an optical rotation of not less than $+58°$ to $+64°$. Ref. ind. at $25°$ 1.473 to 1.476. Contains not less than $4\%$ of aldehydes calculated as citral as determined by the following process.

To 20 grm. of the oil contained in a flask add 20 c.c. $N/2$ solution of hydroxylamine hydrochloride, 8 c.c. of $N$ alcoholic solution of KOH and 20 c.c. of alcohol ($90\%$). Attach a reflux condenser, boil for 30 minutes, cool, and dilute with 250 c.c. of water, rinsing the condensing tube into the flask with part of this quantity. Neutralie the solution thus obtained with $N$. solution of KOH, solution of phenolphthalein being used as indicator, and then titrate with $N/2$ sulphuric acid, a solution of Methyl Orange being used as indicator.

Repeat the experiment, omitting the oil of lemon. The quantity of $N/2$ $H_2SO_4$ required in the second experiment exceeds that required in the first experiment by not less than 10.5 c.c. (Presence of not less than $4\%$ of aldehydes, calculated as citral, $C_{10}H_{16}O$.)

The U. S. P., (9th rev.), requires lemon oil to have an opt. rot. of $57°$ to $64°$, sp. gr. 0.851 to 0.855 at $25°$, and the angle of rotation of the first $10\%$ of distillate to be not more than $5°$ less than that of the original oil. The ref. ind. of this distillate should be not less than 0.002, nor more than 0.0027 lower than that of the original oil.

The ref. ind. of pure lemon oil is usually 1.4750, rarely below 1.4750 and in Parry's experience never below 1.4740.

The sp. gr. of genuine lemon oils ranges between the limits 0.856 to 0.862 rarely 0.854 to 0.863. These figures are but little altered by admixture with turpentine oil or with turpentine and orange oils, but any addition of alcohol will disturb the sp. gr., and may thus be readily detected. Oils of sp. gr. 0.853, such as have recently been met with, were very possibly adulterated with a small quantity of lemon terpenes.

The opt. rot. of the sample and the fractions obtained by distillation are probably the most valuable figures. Pure lemon oils rarely have a rotation outside the limits $+57°$ to $61°$, in rare instances coming within the limits $+56°$ to $+67°$. The figures differ slightly in different years. According to Burgess and Child, some lemon oils at the earlier part of the season may have a rotation of $+68°$, but such are not usually in the market, and are mixed with lemon oil of a lower activity.

In certain seasons the sp. gr. may rarely fall to 0.855, and where only spring lemons are used even to 0.854, and the optical rotation will sometimes be found as low as $+55$.

The average rotation of Palermo oils is a little lower than that of Messina oils. Schimmel & Co. recommend the distillation of 50 c.c. of the oil in a fractionating apparatus, the first 10% distilled (5 c.c.) being examined in the polarimeter. This fraction should have an opt. rot. lower by not more than $5°$ than that of the original oil (Schimmel & Co.). A small quantity of turpentine oil (5%) has very little influence on the optical rotation of the first 10% of the distillate, since the oil of turpentine does not come over to any great extent at this stage. Parry is of opinion that the examination of the rotation of the successive fractions (in 20% quantities) will yield valuable information. The ref. index of the fractions of lemon oil may yield useful information, but the method possesses no advantages over a polarimetric examination.

About 20 to 30% of lemon oil distils between $172°$ and $174°$.

The analytical figures for lemon oil vary considerably at different periods of the pressing, and care should be taken to examine, as far as possible, authentic samples from various districts, pressed at different times, in order to assist one in discriminating between adulterated and merely low-grade samples.

The addition of turpentine oil to lemon oil causes a decrease in rotatory power, but if an admixture of orange terpenes together with turpentine oil has been made, the rotation of the original oil may not be affected. Careful fractional distillation can alone give definite information with respect to these additions. The apparatus employed should be used also for the distillation of some authentic samples of lemon oil, in order to obtain standard results for comparison. Genuine lemon oil always shows a large increase in opt. rot. of the later fractions over the first 10% distilled. The following

CONSTANTS OF PURE LEMON OIL (BURGESS AND CHILD)

| Particulars | Physical constants of original oils | | | Distillation | | | Citral content of 3d fraction |
|---|---|---|---|---|---|---|---|
| | | | | c.c. | Rotation | Zeiss readings, 20° | |
| I. Genuine oil of good quality. (Messina.) | Sp. gr. | = | 0.857 | 10 | +55° 30' | 72.0 | 42% |
| | Rotation | = | +63° 12' | 80 | +70° 40' | 72.4 | |
| | Ref. ind. | = | 1.4755 | 7.5 | +10° 56' | 82.5 | |
| II. Genuine oil (Palermo). Not typical... | Sp. gr. | = | 0.857 | 10 | +54° 6' | 72.2 | 35% |
| | Rotation | = | +61° 27' | 80 | +67° 45' | 72.4 | |
| | Ref. ind. | = | 1.4757 | 7.5 | +19° 13' | 81.5 | |
| III. Genuine oil of very high sp. gr. | Sp. gr. | = | 0.862 | 10 | +50° 41' | 72.0 | 64% |
| | Rotation | = | +58° 30' | 80 | +67° 16' | 72.7 | |
| | Ref. ind. | = | 1.4771 | 7.0 | − 6° 0' | 90.6 | |
| IV. Genuine oil of high sp. gr. | Sp. gr. | = | 0.860 | 10 | +50° 6' | 72.2 | 64% |
| | Rotation | = | +60° 36' | 80 | +68° 43' | 72.6 | |
| | Ref. ind. | = | 1.4769 | 7.0 | − 3° 20' | 88.6 | |
| V. Genuine oil, new crop, 1901 | Sp. gr. | = | 0.858 | 10 | +51° 47' | 71.8 | 40% |
| | Rotation | = | +61° 28' | 80 | +69° 2' | 72.3 | |
| | Ref. ind. | = | 1.4754 | 7.0 | + 8° 14' | 81.9 | |

table, by Burgess and Child (*J. Soc. Chem. Ind.*, 1901, **20,** 1176) gives the constants and behaviour on fractional distillation of 5 samples of genuine oil of lemon. 100 c.c. of oil were distilled in each case.
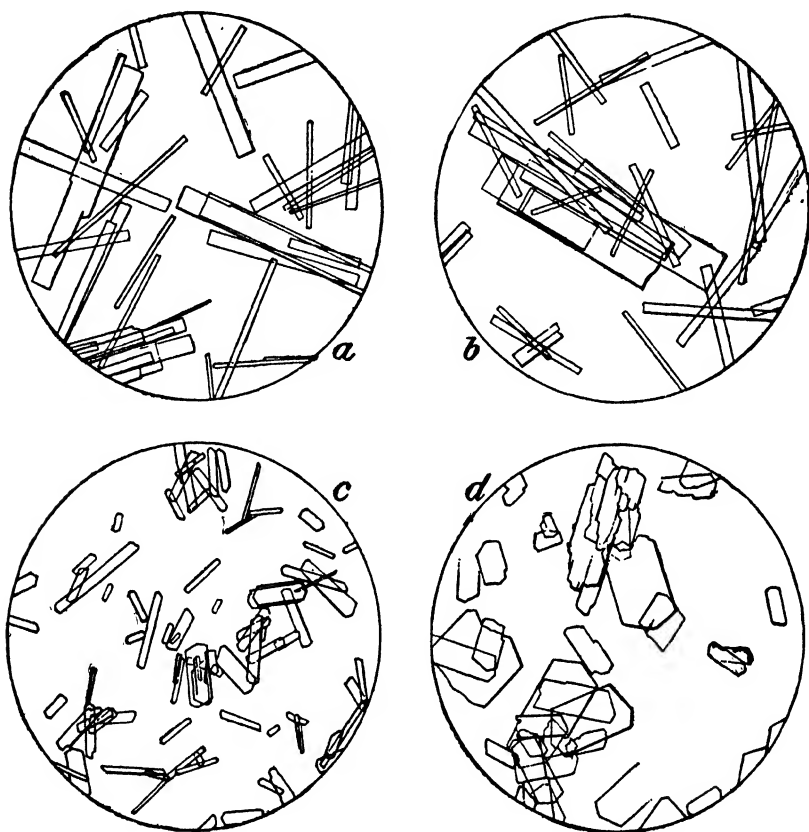


FIG. 1.—Photomicrographs of crystals × 100. *a, b,* Limonene nitrosochloride from pure lemon oil; *c,* limonene nitrosochloride and pinene nitrosochloride from lemon oil mixed with 5 % of oil of turpentine; *d,* pinene nitrosochloride from oil of turpentine. Illustrations from Circular 46, Bur. of Chem., U. S. Department of Agriculture, by E. M. Chace.

## Pinene in Lemon Oil

It having been alleged by importers in the United States that lemon oil may naturally contain appreciable amounts of pinene, the

subject was carefully investigated by the U. S. Bureau of Chemistry, and the results published in Circular 46, Oct., 1909, by E. M. Chace. The investigation showed that genuine lemon oil contains no appreciable amounts of pinene when tested by the following method:

50 c.c. of sample are distilled as described on page 588. The distillate is mixed with an equal volume of glacial acetic acid in a 50 c.c. conical flask and immersed in a freezing mixture. 10 c.c. of ethyl nitrite are added and then, slowly, with constant stirring, 2 c.c. of a cooled mixture of 2 parts of concentrated hydrochloric acid and 1 part of water. The flask is kept for 15 minutes in the freezing mixture, and then the liquid rapidly filtered, a filter-paper disk with vacuum being used. The resulting crystals of limonene nitrosochloride are dissolved in the smallest possible amount of chloroform and reprecipitated with methyl alcohol. The crystals are collected, mounted in olive oil, and examined under a power of about 100 diameters. If the pinene derivative is present, its crystals are easily detected (see Fig. 1).

All pure lemon oil contains a small quantity of pinene, and Parry considers that Chace's method of detecting turpentine in lemon oil must be used with considerable caution. Chace, however, states that, whereas pinene occurs in small quantities in lemon oil he has never known it to be found in an authentic sample by the method described.

A favourite adulterant of lemon oil is a highly purified Greek turpentine, fortified with lemongrass citral. Greek turpentine is obtained from *Pinus halapensis*, and has the following characters:

$$
\begin{array}{ll}
\text{Sp. gr.} & \text{0.861 to 0.486} \\
\text{Optical rotation} & +33° \text{ to } +39° \\
\text{Ref. index} & \text{1.4675 to 1.4705}
\end{array}
$$

The adulteration of lemon oil with orange or lemon terpenes (without addition of turpentine oil) may be inferred from the lowered sp. gr., slightly increased rotation, and in the increase of non-aldehydic constituents. Oils adulterated in this manner have, however, frequently also received an addition of lemon-grass citral. If the oil is distilled *in vacuo*, and the odour of the terpeneless portion observed, the addition of lemon-grass oil or lemon-grass citral will be detected. The optical rotation of this residue may also yield some information. Estimation of the non-volatile matter and of the saponification value of lemon oil will serve for the detection and

determination of added fatty substances. Observation of the ref. index which lies within the narrow limit of 1.473 to 1.475 at 20° is of value.

Lemon oil rapidly deteriorates on keeping. It is best stored in tightly stoppered bottles filled to the neck and kept in a cool, dark place. The turbidity of certain specimens is usually due to a small quantity of water.

## Lime Oil

This oil is obtained either by an expression process (generally by the ecuelle) or by distillation, from *Citrus limetta* (Italian) or *Citrus medica var. acida* (West Indian). The expressed oil is the superior of the two and commands a much higher price. Italian lime oil, which is expressed, not distilled, is of a brownish-yellow colour and has a characteristic fragrant odour of the fruit with a secondary odour of bergamot. Its sp. gr. varies from 0.870 to 0.875, and its opt. rot. from +34° to +40°. It contains linalyl acetate and citral. It also contains a little free linalol, but not more than 3 or 4%. The bulk of the oil consists of the terpene limonene.

The West Indian oil, which is the usual oil of commerce, is obtained from the fruits of *Citrus medica var. acida*, whose juice contains a large quantity of citric acid. The plant is plentiful in Jamaica, Dominica and Tahiti; but the most important plantations are on the island of Montserrat, one of the Antilles. The lime harvest here lasts from September to January, and the chief product is, of course, the lime juice.

It is well known that distilled lime oil is quite different from the hand-expressed oil, the first-named oil having a disagreeable, turpentine-like odour. H. A. Tempany and N. Greenhaigh (*West Indian Bull.*, 1912, **12**, 498), who have investigated the matter, are of opinion that the difference is caused by the loss, during the process of distillation, of part of the lowest and highest boiling fractions. They distilled hand-expressed oils with steam, and obtained an oil with the characteristic turpentine-like odour of the distilled oil of commerce. The highest boiling fractions of the hand-expressed oil contain a blue fluorescent, crystalline substance (perhaps methyl anthranilate), which is absent from the distilled oil. Moreover, citroptene, which ordinarily separates out from the hand-expressed oil when it is left standing, is absent from the distilled oil.

As a rule, the citral-content of the distilled oil is lower than that of the hand-expressed oil.    Authentic samples show the following properties:

I. Hand-expressed oils: $d^{30°}$ 0.8712 to 0.8859, $\alpha_D^{31°}$ + 31.38 to 33.43°, $n_D^{32°}$ 1.4789 to 1.4851, acid value 1.35 to 2.8, citral content 2.2 to 6.6%.

II. Distilled oils: $d^{30°}$ 0.8540 to 0.8858, $\alpha_D^{31°}$ +33.09 to 34.89°, $n_D^{32°}$ 1.4702 to 1.4713, acid value 0.76 to 1.3 citral content 1.2 to 2.0%.

An oil is also distilled from lime leaves, which is yellow in colour and has a lemongrass like odour.    The sp. gr. is 0.877 to 0.878, opt. rot. +37 to +38, aldehydes, presumably citral, 4.3%.

Parry reports on a distilled oil from lime flowers having a sp. gr. 0.870 and an opt. rot. of +21.5°.

## Linaloe Oil

The linaloe oil of ordinary commerce is distilled both in Mexico and Europe from the wood of several species of *Bursera*, chiefly from *Bursera delpechiana* and *Bursera aloexylon*, and is in no way connected with aloe wood, as its name implies (*lignaloe*).    A linaloe wood is also exported from French Guiana and Brazil, but this, known locally as *bois de rose femelle* or *licari* wood, is the product of one of the *Lauraceæ*, probably *Ocotea caudata*.    Its essential oil is known as cayenne linaloe oil, or oil of Bois de Rose.

The principal odoriferous substance of both oils is the alcohol, linalol.    In addition, Mexican linaloe oil has been found to contain geraniol, linalol oxide, methyl-heptenone, a sesquiterpene, two terpenes, methyl-heptenol, terpineol, and myrcene.    Cayenne linaloe oil contains also terpineol, geraniol, methyl-heptenone, methyl-heptenol, nerol, cineole, dipentene and probably myrcene.

The general characters of the two oils usually fall within the following limits:

|  | Mexican | Cayenne |
|---|---|---|
| Sp. gr. | 0.870–0.898 | 0.870 to 0.880 |
| Rotation | −3° to −15° | −10° to −20° |
| Ref. index | 1.460–1.4653 | 1.4610–1.4635 |
| Acid value | 0–6 | 0–1.5 |
| Ester value | 5–42 occasionally to | 3–7 |
| Free alcohols | | 84–94% |
| (Determined in xylene solution). | 75 85–96% | |

Both oils are soluble in 2 to 3 volumes of 70% alcohol. It must be remembered that the estimation of linalol must be carried out with the modifications in the acetylation process described under the estimation of free alcohols, xylene being the best diluent.

The behaviour of the oil on fractional distillation affords a useful indication of the purity and quality of the sample, a high linalol value being indicated by a close similarity in the various fractions constituting the first 90% distilling. A typical sample distilled by Parry and Bennett, having a sp. gr. 0.882 and an optical rotation $-11°$, gave the following results:

| Fraction | % | Sp. gr. | Rotation | Ref. index |
|---|---|---|---|---|
| 1 | 10 | 0 868 | $-11°$ | 1.4580 |
| 2 | 20 | 0.870 | $-11°30'$ | 1.4590 |
| 3 | 20 | 0.871 | $-13°$ | 1.4605 |
| 4 | 20 | 0.872 | $-13°$ | 1.4612 |
| 5 | 20 | 0.876 | $-12°$ | 1.4620 |
| 6 | 10 | 0.913 | . . . . . . . . . . . . . | 1.4750 |

An oil, known as shiu oil, distilled in Formosa from a species of cinnamon (?) contains a large amount of linalol, and may be expected to become an adulterant of linaloe oil, which is largely used in perfumery, and for the manufacture of artificial perfumes.

Shiu oil, however, contains camphor, and as it is very difficult to remove the whole of this, the presence of camphor in linaloe oil may be regarded as indicative of the presence of shiu oil. Schimmel & Co. (*Report*, Oct., 1913, 71) give the following methods for its detection.

**Detection of Camphor by Means of Semi-Carbazide Hydrochloride.**—25 grm. of oil, distilled by steam, are diluted with a mixture of 1 grm. of semi-carbazide hydrochloride and 1 grm. of sodium acetate in 25 c.c. of 90% alcohol. After standing for 24 hours, 1 grm. sodium bicarbonate is added and the whole mass distilled by steam. The distillation-residue is slightly evaporated in a dish on the water-bath and cooled. This causes camphor semi-carbazone to separate out. A little hydrazodicarbonamide (decomposition product of the semi-carbazide hydrochloride) may be found admixed with the latter. The semi-carbazone is now filtered off and dissolved in a little alcohol, the hydrazodicarbonamide remaining undissolved.

When the alcohol has evaporated the camphor semi-carbazone is left; when decomposed with dilute sulphuric acid the latter should develop a clearly perceptible odour of camphor. As a rule the semi-carbazone does not melt very sharply, because the substance is still contaminated with certain other compounds which can only be removed by repeated recrystallisation, but the quantity of the substance available is often insufficient for the purpose.

So small an addition to linaloe oil as 1% of camphor can be traced by the semi-carbazide method, especially when the mixture is allowed to stand for more than 24 hours. But the method is not suitable for quantitative estimation; for example, after one single treatment of a mixture of 80% linalol and 20% camphor only 11% camphor was traceable after an interval of 2 days. The method has, moreover, the great drawback of being very slow.

**Estimation of Camphor by Oxidation with Potassium Permanganate.**—Much better results were obtained by this method, which made it possible to estimate the camphor-content rapidly and with great accuracy.

The *modus operandi* is as follows: Into a distilling flask of 2 litres capacity, 50 grm. of potassium permanganate and 300 c.c. of water are placed; within the course of 30 minutes, 10 grm. linaloe oil are added gradually through a dropping funnel, cooling strongly with ice. The oil is dissolved by warming it. When the action is quite completed and no further warming takes place (after about 2 hours) a further 200 c.c. of water are added, and the unattacked camphor is driven over with steam.

By this method it was possible to detect the addition to linaloe oil of 1% camphor and 10% shiu oil. The manipulation can be carried out in about 4 hours, and the method is also suitable for the quantitative estimation of camphor in linaloe oils which have been adulterated with shiu oils, for which purpose it is necessary to shake out the steam-distillate several times with ether after adding common salt. The ethereal extracts are placed together and the residue is weighed after evaporating the ether.

### Nutmeg Oil

This oil is obtained by the distillation of the nutmeg, the fruit of *Myristica fragrans*. It is colourless or pale yellow. It absorbs oxygen, and becomes darker and thicker on exposure to the air,

The British Pharmacopœia (1914) directs that oil of nutmeg should have a sp. gr. of 0.870 to 0.925, opt. rot. +13 to +30, ref. ind. at 25°, 1.474 to 1.484, soluble in 3 vols. of 90% alcohol, and leave not more than 5% residue on evaporation.

The U. S. P. (10th rev.) states that nutmeg oil should have sp. gr. of 0.859 to 0.924 at 25°, opt. rot. +12° to +30° in a 100 mm. tube at 25°, soluble in 3 vols. 90% alcohol and 1 vol. of 95% alcohol, and leave not more than 5% residue on evaporation. It should form a clear solution with its own volume of 95% alcohol, and a little of the oil evaporated on a water-bath should not leave a residue which crystallises on cooling. This ensures the absence of the fatty oil of nutmeg, which may occasionally be carried over in the distillation. Parry has pointed out that the presence (even in traces) of the fixed oil of nutmeg is said to be objectionable in oil of nutmeg used for the manufacture of *sal volatile*. The residue on evaporation of the oil, after purification with alcohol, consists chiefly of *myristic acid*, melting at 54°.

The limits of sp. gr. for this oil, as laid down by the British Pharmacopœia, are regarded by various observers as being too narrow. Schimmel & Co. give the sp. gr. of oil of nutmeg as 0.865 to 0.925. The ref. index is from 1.478 to 1.4895.

Oil of nutmeg is dextrorotatory, the limits being usually stated as from 8° to 30°, but Power and Salway observed a rotation as high as 38.06° in a sample of genuine oil.

## Mace Oil

This oil is similar to nutmeg oil; indeed, no distinction is made between nutmeg oil and mace oil commercially.

Genuine mace oil is the product of distillation of the arillode of the seed of *Myristica fragrans*. The true oil is colourless, yellowish, or dull red, having a sp. gr. of 0.910 to 0.930 (or, according to Gildemeister and Hoffmann, 0.890 to 0.930). The opt. rot. of the oil is about +10° to +22°. Mace oil is completely soluble in 3 parts of 90% alcohol.

The composition of this oil is very similar to, if not actually identical with that of nutmeg oil.

Nutmeg and mace oils are so similar that they are sold indiscriminately, and it is difficult to obtain authentic samples of either oil.

The oils contain α-pinene, camphene, β-pinene, dipentene, paracymene, d-linalol, terpinenol-4, borneol, d-terpineol, geraniol, safrol, citral-like aldehyde, myristicin, formic acid, acetic acid, butyric acid, caprylic acid, an acid $C_{12}H_{17}OCOOH$, myristic acid, eugenol and iso-eugenol.

The oils are used in perfuming soap, in liqueurs and spices, and as a carminative.

### Orange Oils (Oils of Bitter and Sweet Orange-peel)

The oils of bitter and sweet oranges are obtained by expression from the fresh peel of the fuits of *Citrus bigaradia* and *C. aurantium*, respectively, and are very similar in physical properties and composition. The oil produced from orange-flowers is known as "neroli oil" (page 95).

**Sweet orange** oil is an orange-yellow oil with the characteristic orange odour and an aromatic taste. It consists largely (90%) of dextrolimonene (Wallach). The oil contains in addition the following substances, most of which are present in mere traces or in very small amounts: dextrolinalol (Parry), nonylic alcohol, decylic alcohol, dextroterpineol, normal decylic aldehyde, esters of butyric acid and of its immediately higher homologues (Parry), an ester of caprylic acid, methyl anthranilate or ortho-amino-benzoate (Parry). This substance was found by E. and H. Erdmann and Schimmel & Co. to be present in oil of neroli. It is an oily substance having an odour resembling neroli oil. In solution it possesses a fine characteristic fluorescence; and, according to Flatau and Labbé (*Bull. Soc. Chim.*, [3], 1898, **19**, 361) another aldehyde (of unknown composition), myristicol, and myristinic acid. K. Stephan has isolated an acid similar to, or identical with, cerotic acid. These observers also isolated from sweet orange oil an ester, the acid of which contains 21 atoms of carbon; Parry has isolated this acid, and from an analysis of the silver salt finds that it cannot have a greater molecular weight, if it is monobasic, than 275; this allows only 17 atoms of carbon. It was in the form of an insoluble amorphous powder, melting at 64° to 65°. This compound had a strong odour of oranges.

**Bitter orange** oil is a yellow liquid with a bitter aromatic taste, and a delicate orange odour.

The constituents of sweet orange oil and bitter orange oil are practically identical.

The sp. gr. of sweet orange oil ranges from about 0.848 to 0.853; that of bitter orange oil from about 0.852 to 0.856 at 15°. The sp. gr. is not much altered by adulteration with oil of turpentine, but the addition of alcohol makes a considerable change. The refractive index of sweet orange oil is 1.4728 to 1.4751, that of bitter orange oil 1.472 to 1.4748. The opt. rot. of sweet orange oil is +94° to +99°, and that of bitter orange oil +90° to +95°.

The following physical characters of the oils have been recorded by Schimmel & Co. and Bush & Co.:

|  | Sweet orange oil | | Bitter orange oil | |
|---|---|---|---|---|
|  | S. & Co. | B. & Co. | S. & Co. | B. & Co. |
| Sp. gr. at 15°.......... | 0.848 to 0.852 | 0.8495 to 0.8510 | ............. | 0.853 to 0.854 |
| Opt. rot. at 20°........ | +96° to +98° | +96° to +99° | +92° to +98° | +91° to +94° |

Also the following S. & Co. (Rep., Oct., 1909, p. 66).

|  | Sweet orange oil | | Bitter orange oil | |
|---|---|---|---|---|
|  | Jamaica | Italy | Jamaica | Italy |
| Sp. gr. 15°..... | { 0.8481 0.8488 | 0.8480 0.8530 | 0.8517 0.8521 | 0.8530 0.8570 |
| Opt. rot....... | +97° 47' to 98° 2' | +95° to +98° | +96° 20' to 96° 58' | +90° to +93° |
| Opt. rot. of first 10 c.c....... | +97° 4' to 96° 54' | nearly same | +96° 40' to 95° 53' | slightly higher |
| Residuum..... | 1.4% | 2 to 4% | 2.6 to 3.2% | 3 to 5% |

Orange oil has a high opt. rot. which changes with difference in temp. Hence, in order to obtain comparable data, it is necessary to record the temp. at which the observation was made and to compute the angle of rotation for 20°. For every degree in temperature between +10° and +20° the difference in the angle of rotation is 14.5 minutes. When recomputing for 20° it is necessary, therefore, to deduct 14.5' for every degree in temperature if the observation was made below 20°, and to add 13.2' for every degree in temperature if the observation was made above 20°.

Any adulteration must therefore cause a lowering in this constant. The greatest change is produced by turpentine oil. Lemon oil

lowers the rotatory power to a smaller extent. An addition of lemon or turpentine oil to orange oil raises the sp. gr.

To detect turpentine oil use the method on p. 630.

Oil of sweet orange-peel is official in the United States Pharmacopœia (10th rev.), which directs that it should have an optical rotation of not less than $+94°$, and that the first fractions distilled should give no evidence of the presence of pinene, a sp. gr. at $25°$ of 0.842 to 0.846, ref. ind. 1.4723 to 1.4737 at $20°$. The angle of rotation of the first 10 %of distillate of orange oil must be equal to, or only slightly greater than, that of the original oil.

Pure orange oil begins to boil at about $173°$ to $174°$. Umney found that the pure oil, on fractional distillation, gave 20% of distillate between $173°$ and $175°$; 61% between $175°$ and $178°$; 14% between $178°$ and $188°$; leaving 5% of residue. Admixture with much oil of turpentine will lower the b. p. of the oil.

Jamaican orange oil is now a regular commercial article, and although it differs slightly from Sicilian oil, the two products are very nearly identical. Parry has examined samples of this Jamaican oil, with the following results. A sample of sweet oil had the following characters:

Sp. gr. at $15°$ .................................... 0.850
Optical rotation.................................... $+98° 40'$
Ref. index at $20°$.................................... 1.4719

On fractionation under 12 mm. pressure, the oil gave the following fractions:

10 c.c. of rotation $+ 97° 30'$ and ref. index 1.4709
80 c.c. of rotation $+ 99° 20'$ and ref. index 1.4707
5.7 c.c. of rotation $+ 86° 53'$ and ref. index 1.4705

The total aldehydes present were found to be 1.2%.

Two other samples of West Indian orange oil which were examined under similar circumstances contained 1.3 and 1.4% of aldehydes.

Compared with Sicilian oils, the above figures show no appreciable difference, the figures being practically identical, and the aldehyde value of such oils averaging 1.3%.

Schimmel & Co. (Report Oct., 1915) report on Jamaica, produced oil of sweet and bitter orange giving constants that fall within the prescribed limits.

**Distilled orange oil** is inferior to the expressed oils, owing to the deterioration consequent upon the distillation process, which injures the oxygenated constituents. Schimmel & Co. give the following figures obtained by the examination of 2 distilled oils of orange:

|  | Bitter | Sweet |
|---|---|---|
| Sp. gr. | 0.853 | 0.855 |
| Opt. rot. | +96.97° | +95.95° |

This oil and the residual products from the manufacture of terpeneless oil of orange are occasionally used as adulterants of orange oil. When present in any considerable quantity, both these additions render the colour pale, lower the sp. gr. and affect the odour of the sample. The terpenes of lemon oil are also used as adulterants and have a similar effect.

Oil of orange is acted upon by light and air in the same manner as lemon oil.

The concentrated or *terpeneless oil* of sweet orange is somewhat complex, has a sp. gr. of about 0.900 and an optical rotation of about +10°. At a pressure of 10 mm. terpeneless oil of orange distils between 100° and 150°. Parry found terpeneless oil of orange-pea (immature fruit) to have a sp. gr. of 0.910 and an optical rotation of 6.5°.

Parry has also examined a sample of the essential oil obtained from the peel of the immature fruit of the orange, *i. e.*, when about the size of a pea (orange-pea oil). The oil is interesting, since it forms a connecting link between neroli and the fruit oil. The pea oil was found to contain dextro- and lævolimonene, dextrolinalol, and terpineol, and also a trace of methyl anthranilate, but such a small trace of this compound was present that it is clear almost all had disappeared in the early stage of fructification. The following comparison of the characters of the oil with neroli oil and the fruit oil is instructive. The decrease in sp. gr. and increase in opt. rot. show the gradual increase in the proportion of terpene present:

|  | Sp. gr. | Opt. rot. |
|---|---|---|
| Neroli................................. | 0.870 to 0.880 | $+4°$ to $+15°$ |
| Orange-pea............................. | 0.862 | $+71°$ $15'$ |
| Orange................................ | 0.850 | $+96°$ |

*Mandarin or tangerine orange oil* is expressed from the peel of the fruit *Citrus nobilis* (*C. madurensis*). It is golden yellow in colour with a slight bluish fluorescence.

The sp. gr. at $15°$, 0.854 to 0.859; opt. rot., $+65°$ to $+75°$; ref. ind. 1.475 to 1.478. The angle of rotation of the first $10\%$ of distillate is about the same as the original oil or not over $3°$ higher.

Mandarin oil contains *d*-limonene, dipentene, methyl anthranilate, methyl methyl anthranilate, and traces of an unknown aldehyde. The methyl anthranilate is the compound giving the fluorescence to the oil.

Mandarin oil is used in confectionary and perfumery.

Hesse and Zeitschel (*Ber.*, 1901, **34**, 296) have proposed the following method for the detection and estimation of methyl anthranilate in essential oils, based upon the precipitation of the ester with sulphuric acid, and the subsequent saponification. The oil to be examined is dissolved in 3 parts of dry ether, the solution cooled at least to $0°$, and a cold mixture of 1 vol. of strong sulphuric acid with 5 vols. of ether is added, drop by drop, with continual stirring, until no further precipitate forms. The precipitate is washed with dry ether until odorless and it is brought into solution by means of water plus a little alcohol, if necessary, and the liquid titrated with $N/2$ alkali, with phenolphthaleïn. The solution is then saponified by boiling with excess of alcoholic potassium hydroxide for 30 minutes. The quantity of methyl anthranilate may be calculated from the acid value of the ester sulphate. (It is unsafe to weigh the ester sulphate, owing to its ready dissociation.) If the precipitate contains principally the methyl-anthranilic sulphate or analogous compounds, the amounts of alkali used in the 2 operations will be as 2 : 1. If less is required in the saponification than is given by this ratio, unsaponifiable bases are indicated. These may be extracted by ether from the alkaline solution. Anthranilic acid is

obtained by evaporating the liquid, acidifying with acetic acid, and extracting with ether. It may be identified (and its purity confirmed) by the m. p. alone and after grinding with pure anthranilic acid.

If a large quantity of the sulphate precipitate is obtained, it may be dissolved as above, and an aliquot part of the solution taken for the titration and saponification. A few drops of sulphuric acid are added to the main portion of the aqueous solution, which is then shaken once with petroleum spirit to remove resins. Sodium carbonate solution is added, the precipitate dissolved in ether and the methyl anthranilic hydrochloride precipitated by passing a current of dry hydrochloric acid gas through the solution. The hydrochloride is purified by solution in methyl alcohol and precipitation by ether. Other bases forming soluble hydrochlorides will be found in the ethereal solution. The ethereal liquid from the original sulphate precipitate is washed with water to remove excess of sulphuric acid, and the ether removed. The liquid may then be used for the detection and estimation of other constituents present in the oil, which will remain unaffected in the above process.

The following method for the detection and estimation of methyl anthranilate is due to E. Erdmann (*Ber.*, 1902, **35,** 24). The process depends upon the formation of an azo-dye when methyl anthranilate, the only primary base as yet known to occur in essential oils, is diazotised in the presence of an aromatic phenol, such as $\beta$-naphthol. When only very small quantities of the ester are present, a colorimetric modification of the method is employed, a sufficient amount of an aqueous solution of $\beta$-naphthol-disulphonic acid R being added to the solution of the ester after diazotisation, and the tint obtained compared with a standard solution of methyl anthranilate when quantitative results are required. In the case of larger amounts of the ester, Erdmann prefers to dilute the diazotised solution of the ester (obtained by treating its hydrochloric acid solution with sodium nitrite for 10 minutes) to a known volume, and then titrate with it 0.5 grm. $\beta$-naphthol dissolved in a dilute solution of sodium hydroxide to which some sodium carbonate is subsequently added, made to approximately 10 c.c. volume, the end-reaction being observed by "spot" tests, or by filtering a small portion of the liquid and testing it with the diazo-compound and with the naphthol solution. The insoluble orange-coloured dye produced falls to the

bottom of the vessel, and the titration is finished when no diazo reaction is obtained either by the addition of a few drops of the diazo solution or of the $\beta$-naphthol solution to a little of the filtrate from the titrated liquid. A few mg. of methyl anthranilate may thus be estimated, and the presence of the corresponding compound of methyl-anthranilic acid does not interfere. The colouring matter above noted dissolved in strong sulphuric acid gives a reddish-violet solution.

The detection of methyl anthranilate by producing a *quinazoline* derivative has been described by P. Freundler (*Bull. Soc. Chim.*, [3], 1904, 31, 882).

A *South American orange oil* has been examined by Umney and Bennett (*Brit. and Col. Druggist*, 1904, 45, 169), who found it to more closely resemble orange-leaf than orange-flower oil. The odour was very pleasant, and suggested a superior petitgrain oil. As examined by Umney and Bennett, South American orange oil has a sp. gr. of 0.887, an opt. rot. of $+2°$ in 100 mm. tubes, and contains 67 % of total alcohols (as geraniol), of which 38 % are free and 35.5 % exist as esters (linalyl acetate). The oil contains lævo-pinene, dipentene, furfural, geranyl acetate, linalol and geraniol, terpineol (?) and traces of methyl anthranilate. On fractional distillation at ordinary pressure, 75 % of the oil distils between 190° and 220°. The oil is readily soluble in 2 vols. of 70 % alcohol. For soap and other perfumery purposes, this oil compares favourably with French petitgrain oil.

For the detection of turpentine in orange oil the b. p. and opt. rot. of the lowest boiling fraction of the oil, fractionated repeatedly with the aid of a dephlegmator, reveal the presence of pinene. This can also be converted into its nitrosochloride and this either into the nitrobenzylamine or nitrolpiperidine base.

The decylic aldehyde content can readily be estimated by means of phenylhydrazine. (See det. of citral, p. 525, for method.)

*California Orange Oil:* Oil from oranges grown in California is now of economic importance. This oil is being produced both by pressing and by distillation.

The California pressed orange oil is readily distinguished by its deep orange red colour and its fine fruity orange aroma. The following table gives the characteristics of authentic pressed oils secured at various times:

| Sp. gr. at 25° | Opt. rot. at 25° | Ref. Ind. at 20° |
|:---:|:---:|:---:|
| 0.8456 | +97.04 | 1.4733 |
| 0.8441 | +98.40 | 1.4731 |
| 0.8441 | +94.08 | 1.4725 |
| 0.8449 | +97.38 | 1.4731 |
| 0.8445 | +98.12 | 1.4729 |
| 0.8447 | +97.70 | 1.4727 |
| 0.8440 | +97.68 | 1.4728 |
| 0.8445 | +98.14 | 1.4728 |

The California distilled orange oil is lighter in colour and possesses an aroma quite different from the pressed oil. This aroma is distinctly characteristic of the distilled product. The following table gives the characteristics of authentic distilled oils secured at various times.

| Sp. gr. at 25° | Opt. rot. at 25° | Ref. Ind. at 20° |
|:---:|:---:|:---:|
| 0.8429 | +99.56 | 1.4726 |
| 0.8417 | +99.20 | 1.4721 |
| 0.8424 | +99.66 | 1.4722 |
| 0.8441 | +98.72 | 1.4721 |
| 0.8435 | +97.94 | 1.4721 |
| 0.8430 | +99.06 | 1.4721 |
| 0.8432 | +98.54 | 1.4721 |
| 0.8431 | +98.34 | 1.4722 |

## Petitgrain Oil

Petitgrain oil is derived from the leaves, twigs, and usually also the immature fruit of the bitter orange (*Citrus bigaradia*) by distillation with water. The best petitgrain oil is distilled in the south of France, a certain amount in Algeria and Spain, and a large amount of less perfume value in Paraguay. This latter forms the bulk of the oil of commerce.

An oil known as "petitgrain citronnier" is obtained from the twigs, leaves, and unripe fruit of the lemon tree (*Citrus medica*). The oil has an odour similar to that of petitgrain oil, but recalling lemon. Petitgrain citronnier has a sp. gr. of 0.868 to 0.874 or higher, an opt. rot. of $+13°$ to $+34°$, and a saponification value of 14.5 to 32.2. It contains citral and linalyl acetate.

"Petitgrain mandarin" is obtained similarly from *Citrus maduren-sis*. The oil has an optical rotation of $+6.25°$ and contains about 45% of esters, calculated as linalyl acetate.

Petitgrain oil is a yellowish oil with an aromatic and slightly bitter taste, and an odour similar to that of neroli oil, though far less delicate than the latter. Petitgrain oil is completely soluble in 2 volumes of 80% alcohol, and usually in 3 to 4 volumes of 70%.

The sp. gr. of petitgrain oil usually ranges from 0.885 to 0.900, though some samples may fall to 0.882. French oils have generally a lævorotation, but those from Paraguay are mostly dextrorotatory. The limits are about $-1°$ to $+4°$ or $+5°$. The oil has a saponification value of 110 to 245, equivalent to 38 to 85% of ester calculated as linalyl acetate. The ref. index is about 1.4650.

Petitgrain oil as usually met with (*i. e.*, derived from the leaves, twigs, and immature fruit) contains, among other substances, dipentene, dextrolimonene, furfural, lævolinalol (25 to 35%), nerol, geraniol, dextroterpineol (m. p. 35°), linalyl acetate (50 to 75%), geranyl acetate, neryl acetate, methyl anthranilate (small amount), a sesquiterpene, and a pyrrol derivative. Oils which have been obtained from the leaves and twigs (only) of the plant contain little or no limonene. Petitgrain oil obtained only from the leaves of the tree contains 70 to 75% of linalol, 10 to 15% of geraniol, and a small proportion of a sesquiterpene.

Gildemeister and Hoffman (*The Volatile Oils*, 2nd ed.) give the following properties of petitgrain oils from various sources.

| Source | $d_{18°}$ | $\alpha_D$ | % ester |
|---|---|---|---|
| Calabria.................... | 0.8746 | $+18°$ | 26.3 |
| Spain...................... | 0.8849 | $+8.45$ | 28.6 |
| Comores.................... | 0.8664 | $+42.75$ | 10.9 |
| Jamaica.................... | 0.8846 | $+6.5$ | 28.7 |
| West Indies................ | 0.8531 | $+43.5$ | 2.1 |
| S. America................. | 0.8870 | $+2$ | 36.5 |
| Syria...................... | 0.8857 | $+3.45$ | 27.1 |

A number of parcels of petitgrain oil have been found, during the last few years, to have a somewhat low ester value and a high optical rotation. This is probably due to the more or less careless selections

of the material to be distilled, in which some young fruits, more mature than usual, have been included. The ester value of such oils falls to 35%, and the optical rotation rises to $+9°$. A sample of petitgrain oil, of authentic origin, distilled in Jamaica (*Bull. Imp. Instit.*, 1913, **11**, 437) has been found to have a rotation of $-6° 45'$.

Terpinyl acetate has recently been found as an adulterant of this oil. The following results are obtained on the analysis of several samples of petitgrain oil so adulterated. The analyses are by Parry and by Messrs. Schimmel & Co.

| | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| $d^{15}$ | 0.9019 | 0.8968 | 0.8917 | 0.8905 |
| $\alpha_D$ | $+4° 47'$ | $+1° 40'$ | $+2° 56'$ | $-12° 0'$ |
| Solubility | 5 vol. & m. 70 % alc. dilute sol. opal. | 3 vol. & m. 70 % alc. | 1 vol. & m. 80 % alc. dilute sol. opal. | Any vol. 90 % alc. |
| Acid value | 2.3 | 0.3 | 0.5 | 0.5 |
| Ester value after 1 h. sap. with 10 c.c. N/2 alkali | 111.2 | 112.4 | 136.8 | 84.0 |
| Ester content (calc. as linalyl acetate) | 38.9% | 39.4% | 47.9% | 29.4% |
| Ester value after 2 h. sap. with 20 c.c. semi-normal alkali | 119.3 | 121.8 | 138.5 | 89.0 |
| Ester value after 1 h. sap. with 10 c.c. semi-normal alkali + 25 c.c. alc | 102.3 | 99.7 | 133.5 | 80.5 |
| Difference | 17.0 | 22.1 | 5.0 | 8.5 |
| Sap. value | 113.5 | 112.7 | 137.3 | ............ |
| Acid value II | 107.6 | 112.4 | 128.4 | ............ |
| Difference | 5.9 | 0.3 | 8.9 | ............ |
| Terpinyl acetate content about | 9 % | 12 % | ............ | ............ |

Petitgrain oil is adulterated with turpentine, lemon oil and orange oil. These adulterants lower the sp. gr., the solubility and change the angle of rotation. Other adulterants which have been observed more difficult of detection are ethyl tartrate, oleic acid and terpinyl acetate.

Petitgrain oil is used as a source of nerol and in perfumery, especially in *eau-de-cologne*.

## Orange-flower Oil (Neroli Oil)

This oil is obtained by the distillation of the flowers of the bitter orange, *Citrus bigaradia*, with water. It is really the oil that separates directly from the water in the distillate (without cohobation),

and is a by-product in the manufacture of orange-blossom water, which latter is official in the B. P. and U. S. P.

Neroli oil is yellowish, slightly fluorescent with a powerful odour of orange-blossoms, and a bitter aromatic taste. It becomes brownish-red on exposure to light for some time. When strongly cooled, it becomes turbid by the separation of a stearoptene, termed by Boulay, in 1828, "neroli camphor." It is an odourless and tasteless paraffin melting at 55°.

Neroli oil has a sp. gr. ranging from 0.870 to 0.880 (usually 0.870 to 0.875), and is slightly dextrorotatory, about +1.5° to +5.0°, or slightly higher. The ref. ind. is 1.468 to 1.474. It is soluble in 1.5 to 2 volumes of 80% alcohol, the resulting solution having a violet-blue fluorescence (due to methyl anthranilate). The addition of more alcohol to this solution causes a turbidity, and crystalline flakes of the paraffin separate out. The physical properties of neroli oil, together with a comparison of the odour with oils of known origin, are valuable data in judging of purity.

An oil produced by the simple distillation of the flowers of *Citrus aurantium*, sometimes termed "*sweet neroli oil*" or *Portuguese neroli oil*, is occasionally met with, though the commercial specimens of the oil sold under these names are usually derived from a mixture of various aurantiaceous oils. A sample of the true "sweet neroli oil" distilled in Germany had a sp. gr. of 0.893 and an optical rotation of +16.1°. It is a dark yellow oil having an odour altogether unlike the true neroli and orange oils.

Commercial oil of sweet orange-flowers has a sp. gr. of 0.860 at 23°, and an optical rotation of about +30° at the same temperature. one sample contained 6.35% of esters (as linalyl acetate), and no methyl anthranilate could be detected. According to E. Theulier, the oil contains, in addition to esters, dextrocamphene, dextrolimonene, dextrolinolol, and a paraffin.

The *constituents* of neroli oil comprise limonene; camphene; lævopinene; dipentene; lævolinalol (20 to 25%); geraniol; nerol; farnesol; dextroterpineol (m. p. 35°); dextronerolidol (6%); linalyl, geranyl and neryl acetates (7 to 18%); esters of phenyl-acetic acid; benzoic, acetic, and palmitic acids (traces); methyl anthranilate (0.7%); indol, and a paraffin. The odour of the oil and its characteristic fluorescence are largely due to the presence of methyl anthranilate.

*Nerol* and *nerolidol* are alcohols identified by Hesse and Zeitschel in neroli and petitgrain oils. Nerol is isomeric with geraniol, and possesses a delicate odour of roses. It does not combine with calcium chloride, as does geraniol. Nerolidol is a sequiterpene alcohol, probably belonging to the aliphatic series. It has a feeble odour and the low sp. gr. of o.88o.

*Indol* and *methyl anthranilate* have been shown by Hesse and Zeitschel to be present in orange-flowers, and they are thus not accidental products of the process of manufacture.

*Methyl ortho-amino-benzoate*, or methyl anthranilate, was discovered in neroli oil by E. and H. Erdmann and Schimmel & Co., and is an oil which crystallises on cooling. This substance has been found by Parry in bitter orange oil, the crystals melting at 23° to 25°. It is interesting as being almost the only nitrogenous constituent of essential oils possessing a sweet odour. The artificial neroli oil of commerce consists chiefly of methyl anthranilate with several alcohols, and is a frequent adulterant of the natural oil. Nerolin, a crystalline synthetic substance, is $\beta$-naphthol-methyl-ether.

The *adulterants* most usually found in neroli oil are the oils of bergamot and petitgrain. Since linalol and linalyl acetate are characteristic constituents of all these, the detection of them in neroli oil is rendered somewhat difficult. Oil of bergamot, however, usually contains from 35 to 45% of esters, with a corresponding saponification value of 100 to 130, while petitgrain oil contains 35 to 85% of esters, with a corresponding saponification value of 110 to 245. Genuine neroli oils shows a saponification value ranging from 20 to 52, corresponding to 7 to 18% of esters, but good oils usually have saponification values lying between 35 and 45, equivalent to 12 to 15% of esters (as linalyl acetate). Thus an oil having a saponification value exceeding 55 should be regarded as suspicious. The acetyl value of neroli oil is about 160, equivalent to 35 to 38% of free alcohols.

It is probable that an appreciable saponification of the esters of neroli oil (to the extent of 5 or 6%) takes place during distillation, as is known to occur in lavender oil distillation (Jeancard and Satie, *Bull. Soc. Chim.* [3], 1900, **23**, 605).

Distilled oil of orange, distilled over orange-blossoms, is also fairly frequently met with as an adulterant of neroli oil.

The proportion of stearoptene present in neroli oil depends upon the extent to which the distillation of the blossoms is carried, the later fractions of the distillate containing most of the paraffin. The adulteration of neroli oil with stearoptene-free oils of course lowers the content of stearoptene and thus the strongly cooled oil may not become turbid, as would be the case with an oil containing a normal amount of the paraffin. This fact has been employed as a test for the genuineness of neroli oil.

**Chinese neroli oil** is stated to be derived from *Citrus triptera* (*Trifoliata*). An examination of this oil by Umney and Bennett (*Pharm. J.* [4], 1902, **15,** 146) showed that it is of a yellowish-brown colour, becoming paler on exposure to light. It has a sweet odour and is slightly fluorescent, especially in alcoholic solution. The sp. gr. of Umney and Bennett's sample was 0.850, and it had an opt. rot. of $+35°$. The oil contained 4.8% of esters calculated as linalyl acetate, and 21.4% of free alcohols (as linalol). It consisted chiefly of limonene, linalol, traces of linalyl acetate, methyl anthranilate, and a paraffin.

**Orange-flower water** is usually obtained by the distillation of the flowers either with steam or water over an open fire. Neroli oil and orange-flower water are obtained. The water reproduces the odour of the flowers much better than the neroli oil.

About one-third of the odoriferous constituents (the most valuable) of the blossoms pass into the water. Except for the terpenes, orange-flower water contains the same constituents as neroli oil, together with esters of phenyl-ethyl alcohol and, possibly, phenyl-aceto-nitrile. The proportions of free alcohols and of methyl anthranilate are much higher in the oil contained in orange-flower water than in neroli oils, while the esters of the terpene-alcohols are much less in amount. Orange-flower water is official in the B. P. and U. S. P.

## Parsley Oil

This oil may be obtained by the distillation of any part of the common parsley herb (*Petroselinum sativum*). It is usually distilled from the seeds, but the finest oil is that obtained from the green herb.

The characters of parsley oil as obtained from different parts of the herb are shown in the following table. The specific properties and composition of French oil of parsley are also included:

| Source | Sp. gr. | Opt. rot. | Other characters and constituents |
|---|---|---|---|
| Seeds.......... | 1.05 to 1.10 | −5° to −10° | A colourless, yellowish or yellow-green thick oil, containing lævo-pinene and apiole. |
| Herb.......... | 0.902 to 1.015 | +1.25° to +4.15° | Thin greenish-yellow oil, containing about 20 % apiole. |
| Dried root..... | 1.049 to 1.101 | ................ | Apiole crystallises out at ordinary temperatures. |
| French oil...... | 1.017 | +1.4° to −5.7° | Palmitic acid; mixture of several phenols; pinene; myristicin; apiole. Myristicinic acid formed on oxidation. |

Parsley oils containing much apiole (frequently called "parsley camphor") often become semi-solid, or deposit crystals, at the ordinary temperature. The apiole can be crystallised out from any oil containing it by cooling to a low temperature.

Apiole has the constitution of a dimethyl-methylene-ether of allyl-tetroxy-benzene. An isomer of this substance, dill-apiole, is present in oil of dill. The constitution and characters of these substances are discussed on pp. 505 *et seq.*

Parsley oil has been found by Mourgnes and by Bignami and Testoni (*Pharm. J.* [4], 1900, **11**, 313; *Pharm. Zeit.*, 1900, **45**, 606) to contain another constituent or mixture of constituents, to which Mourgnes gave the name "cariol." According to Bignami and Testoni, about 50% of this substance consists of a compound possibly identical with the "myristicin" found by H. Thoms to be the chief constituent of French parsley oil (with some apiole), apiole being, according to this observer, the preponderating constituent of German parsley oil. Thoms considers this compound, isolated by him from French parsley oil, to be true myristicin, while the similar compound in mace oil he regards as *iso*-myristicin.

Parsley oil is used as a source of apiole, medicinally and as a spice.

## Peppermint Oil

The English and American forms of this oil, which is official in the British and American Pharmacopœias, are obtained by the distillation with steam of the flowering herb *Mentha piperita*. The English oil is prepared from the green herb, while the best kind of American oil is frequently obtained from the dried or partially dried herb. Japanese and Chinese oils of peppermint are derived from *Mentha arvensis*.

The following details in regard to peppermint have been given by Camus. (*Report of Roure Bertrand Fils*, Oct., 1911, 3.)

*Mentha piperito* does not constitute a separate species, but is a hybrid of *Mentha viridis* and *Mentha aquatica*. It may be regarded as a sterile plant, as it fruits rarely, and even then the fruit is mostly badly developed; hence the plant must be propagated by subdividing the rhizomes. Like all *Mentha* species, *Mentha piperita* is extraordinarily variable. To add to the confusion, different varieties are cultivated in various plantations under the common denomination of "peppermint." Several varieties also occur of the original species. *Mentha piperita* embraces 2 groups; group I including the sub-species *piperita*, Briq. with numerous varieties, while group II includes the sub-species *citrata*, Briq., which under the name of "citronella" is much grown in France because of its pleasant aroma, but does not appear to be used commercially. In its internal structure *Mentha piperita* exhibits certain features midway between those of *Mentha viridis* and *Mentha aquatica*. How variable are the *Mentha*-species is shown by *Mentha viridis*, L. and *Mentha aquatica*, L.; for the authors describe no fewer than 6 varieties of the former, and as many as 8 of the latter, besides indicating many others.

The following figures are obtained from the ordinary oil, and the oil distilled from the so-called "red" peppermint, which has only recently been cultivated in France.

|  | Ordinary peppermint | | Red peppermint | |
| --- | --- | --- | --- | --- |
| d$^{15°}$ | 0.9191 | 0.9184 | 0.9170 | 0.9136 |
| a$_D$ | $-10°\ 54'$ | $-8°\ 2'$ | $-16°\ 38'$ | $-13°\ 44'$ |
| Solubility in 80 % alcohol | 1 vol. afterwards clouding | ............ | 1 vol. afterwards clouding | ............ |
| Acid value | 0.8 | 0.8 | 1.0 | 1.2 |
| Ester value | 40.5 | 31.7 | 18.9 | 17.5 |
| Menthyl acetate | 14.3 % | 11.2 % | 6.7 % | 6.2 % |
| Ester value after acet | 160.8 | 169.1 | 180.2 | 185.6 |
| Total menthol | 50.9 % | 53.9 % | 58.0 % | 60.0 % |
| Free menthol | 39.6 % | 45.1 % | 52.8 % | 55.1 % |
| Proportion of menthone | 7.3 % | ............ | 16.8 % | ............ |

Two varieties of the herb—known as black and white mint—are used in England for the production of oil of peppermint. The black mint is the coarser kind and yields more oil, of somewhat less delicate aroma, than the white mint. Peppermint oil is much used in medicine and pharmacy, and in the preparation of confectionery and liqueurs.

J. C. Umney found 2 oils from "black" and "white" mint to have the following characters:

| Source | Sp. gr. | Opt. rot. | Menthol, % | | Menthone, % |
|--------|---------|-----------|------------|------------|-------------|
| | | | Free | Combined | |
| Black mint.......... | 0.9036 | $-23.5°$ | 59.4 | 3.7 | 11.3 |
| White mint.......... | 0.9058 | $-33°$ | 51.9 | 13.6 | 9.2 |

The B. P. describes peppermint oil as colourless, pale yellow, or greenish-yellow and directs that the oil should have a sp. gr. of 0.900 to 0.920, and should dissolve in 4 volumes of 70% alcohol, and the opt. rot. must be between $-20°$ to $-35°$. The oil must contain not less than 50% total alcohols (free and combined), calculated as menthol, and not less than 5% of esters, calculated as methyl acetate.

English oil of peppermint is probably the finest in odour, although certain German distillates approach it in this respect. The odour and taste of the oil are very good guides to its quality. Peppermint oil improves in odour on keeping, even for many years. Japanese oil of peppermint is, at the ordinary temperatures, frequently a mass of crystals (menthol) saturated with oil.

American oil of peppermint is the only variety of this oil the composition of which is at all fully known, but so far as the other kinds have been examined, they have been found to closely resemble the American, and this is especially the case with the English oil. American oil of peppermint was the subject of an exhaustive research by Power and Kleber (*Arch Pharm.*, 1894, **232**, 639), who found it to contain the following substances: menthol, menthyl acetate, menthyl isovalerate, a menthyl ester, menthone, acetic aldehyde, acetic acid, isovaleric aldehyde and acid, inactive pinene, lævolimonene, phellandrene, cadinene, cineole, a lactone, traces of amyl alcohol and dimethyl sulphide, and some unstable high-boiling sulphur compounds. In addition, peppermint oil possibly also contains liquid isomeric menthols. The composition and quality of the oil are considerably influenced by the climate and soil, and the cultivation methods employed.

Japanese peppermint oil has been found to contain $\Delta'$-menthenone, a ketone not hitherto found in essential oils (*Schimmel's Report*, Oct., 1910, 97).   Lævo-limonene, which Power isolated from American oil has been found by Murayama (*J. Pharm. Chim.*, 1910, *vii*, 1, 549) in Japanese oil.   Messrs. Schimmel & Co. (*Report*, April, 1912, 103) have identified *d*-ethyl-*n*-amylcarbinol as a constituent of the Japanese oil.   Neo-menthol is also present in this oil (Pickard and Littlebury, *Trans.*, 1912, **101**, 109).   Walbaum (*Jour. Prakt. Chem.*, 1917, **96,** 245) has isolated 3-hexenol − 1-1 phenylacetate.   Schimmel and Co. (*Report*, 1918) report the occurrence of $\beta$-$\gamma$-hexanol ester of phenylacetic acid.   Thoms has carried out a series of experiments on the cultivation of the Japanese plant at Dahlem near Berlin and in German South West Africa.   The characters of the oils obtained are compared in the following table with those of normal Japanese distilled oil.

|  | Old Jap. oil (dist. in Japan) | Oil from herb grown in German S. W. Africa | Oil from herb grown at Dahlem (summer 1911) |
|---|---|---|---|
| Sp. gr. | 0.9043 (18°) | 0.9032 (22°) | 0.8954 (22°) |
| $\alpha_D$ | −35.25° (23°) | −35 (24°) | −34.75° (25.5°) |
| Acid value | 4.05 | 2.99 | 4.01 |
| Ester value | 27.73 | 4.68 | 12.744 |
| Ester value after acet. | 289.5 | 304.8 | 283.25 |
| Esterified menthol | 7.74 | 1.302 % | 3.546 |
| Free menthol | 72.77 | 83.528 % | 75.271 |
| Total menthol | 80.51 | 84.830 % | 78.817 |
| Sol. p. | cannot be determined | +20 to 20.5° | +14.5° |

Conversely, Shinosaki (*J. Ind. Eng. Chem.*, 1913, **5,** 656) has examined oils distilled from German and English plants grown in Japan.   The following are the figures which these oils gave on analysis.

| Oil from | Japanese herb | German herb | | English herb | | German herb from Okayama |
|---|---|---|---|---|---|---|
|  |  | 1910 | 1911 | 1910 | 1911 |  |
| $d^{15°}$ | 0.8989 | 0.9638(?) | 0.9105 | 0.9228 | 0.9132 | 0.9161 |
| $\alpha_D$ | −28.92° | .......... | −42.25° | −52.25° | −63.60° | −18.15° |
| $n_D^{18}$ | 1.4602 | 1.4671 | 1.4672 | 1.4717 | 1.4573 | ......... |
| Acid value | 0 | 19.53 | 0 | 4.42 | 7.06 | 3.45 |
| Menthyl acetate | 6.35 | 24.94 | 11.08 | 26.50 | 13.65 | 8.36 |
| Total menthol | 69.30 | 85.71 | 66.30 | 66.88 | 75.60 | 58.61 |
| Sol. in 70% alcohol at 20° } in vols. | 2.8 | 2.5 | insol. 15 | insol. 15.3 | | insol. |

In regard to the botanical origin of the Japanese peppermint plant, differences of opinion exist. For details of these, a paper by Holmes (*Perf. and Ess. Oil Record*, 1913, 4, 32) should be consulted.

The experimental station for medicinal plants attached to the Royal Hungarian Agricultural Academy at Klausenburg-Kolozsvár has examined a series of peppermint oils distilled in Hungary.

The Hungarian peppermint oil resembles the American oil closely. The plant yields 1.17% oil, possessing the following constants: $d^{15°}$ 0.90142 to 0.91918, $\alpha_D$ $-26.72°$ to $-32.38°$, $n_D^{20°}$ 1.4632 to 1.4760, soluble in 3 to 5 parts 70% alcohol and in its own volume of 90% alcohol. The following fractions passed over during distillation: up to 200° 7.0%, 200 to 205° 10.3%, 205 to 210° 13.4%, 210 to 215° 12.9%, 215 to 220° 16.7%, 220 to 225° 11.6%, 225 to 235° 16.4%.

P. Charabot has shown that during the development of the peppermint plant, an oil rich in menthol is first formed containing only a little ester and menthone. Later, the development of the green parts causes a diminution in the total menthol in the oil, while the esters increase in the leaves and diminish in the flowering part of the plant. Finally the menthone increases in the flowers by the oxidation of menthol. The esterification is confined to the green parts of the plant.

The *sp. gr.* of pure English oil of peppermint is generally well within the British Pharmacopœia limits, ranging usually from 0.900 to 0.912. Some pure specimens exceed these narrow limits, while very rarely a sp. gr. of 0.925 is reached. American oils have sp. gr. ranging from 0.896 to 0.908, while the density of French oils ranges from 0.918 to 0.930, German oils from 0.900 to 0.915, and Italian oils and from 0.905 to 0.926. Japanese oil from *Mentha arvensis* has usually a sp. gr. of 0.895 to 0.900 at 24°.

The *opt. rot.* of English peppermint oil usually ranges from $-23°$ to $-32°$ (United States Pharmacopœia limits = $-25°$ to $-33°$ at 25°) falling very rarely to $-10°$ or lower. The rotation in the case of South Italy oils is from $-2°$ to $-27°$, French oils from $-5°$ to $-35°$ and greatest with the Japanese variety (up to about $-43°$). This constant is of much value in conjunction with sp. gr. for the detection of adulteration. The ref. index varies with the source of the oil from 1.458 to 1.469.

Valuable figures relating to the physical characters and chemical composition of the various peppermint oils of commerce have been

recorded by J. Lifschitz (*J. Soc. Chem. Ind.*, 1901, **20**, 151); Italian oils, C. E. Zay (*Chem. Centr.*, 1903, **1**, 331); while Umney and Bennett have described the characters of Sicilian oils obtained from the black Mitcham peppermint herb grown in Messina (*Chem. and Drug.* 1905, **67**, 945).

The solubility test for peppermint oil described in the British and U. S. Pharmacopœias is not always fulfilled by pure oils (p. 107). Many samples will dissolve in 4 volumes of 70% alcohol with, at most, a trifling opalescence. All peppermint oils are soluble in half or more volumes of 90% alcohol.

The U. S. P. requires peppermint oil to be rectified and free from dimethyl sulphide, the presence of which may be recognised by the formation (after a short time) of a white film at the zone of contact when the first c.c. of distillate from 25 c.c. of the oil is poured on to a little mercuric chloride solution.

The normal composition and properties of the chief varieties of peppermint oil are given in the table on page 107. Japanese oil contains naturally a very high proportion of menthol—frequently as much as 85%—and dementholised (or partially dementholised) Japanese oil (by freezing) is sold sometimes as such, and sometimes as the pure oil. Dementholised Japanese oil has a sp. gr. of c.895 to 0.905 at 15°. English peppermint oil contains about 55 to 70% of menthol (free and combined), or somewhat more than the proportion found in most American oils. With Japanese oils, a considerable separation of menthol takes place at the ordinary temperature. American oil generally sets quite solid when placed in a freezing mixture, while English and German oils usually only deposit crystals after long standing in a freezing mixture. The U. S. P. (9th Rev.) requires peppermint oil to contain at least 5% of ester (as methyl acetate) and 50% of total menthol (free and combined), when assayed by the saponification and acetylation processes.

Owing to its importance and high price, peppermint oil is extensively adulterated. An examination of the physical constants of the oil will serve to detect such additions as alcohol, and turpentine and some other oils. All adulterants cause a diminution of the menthol content, which should therefore be estimated. The methods for the estimation of the free and combined menthol, by saponification and acetylation, and for the estimation of menthone, by reduction with sodium to menthol and the subsequent estimation of the

alcohol formed, are fully described on page 593. The alcohol solubility figures are valuable, since it is frequently possible to ascertain the source of the oil by their means. In many cases where the oil is insoluble in 70% alcohol, a low menthol content will be found. It has been stated that some oils, otherwise pure, have received an addition of menthol itself, which is frequently cheaper than oil of peppermint.

The behaviour of peppermint oils on distillation is a useful test as to genuineness. The published data differ to some extent, being influenced according to the method of distillation employed. All genuine oils will yield a considerable fraction distilling in the neighborhood of 215°, since menthol boils at 212°. The following is a summary of the results of distillation (50 c.c.) of 17 pure peppermint oils from various sources, recorded by Schimmel & Co.:

| Temperature | Distillate, % |
|---|---|
| Up to 200° | 1.0 to 8.8 |
| 200°–205° | 0.6 to 19.2 |
| 205°–210° | 2.4 to 26.8 |
| 210°–215° | 13.0 to 49.4 |
| 215°–220° | 6.4 to 34.4 |
| 220°–225° | 0 to 23.6 |
| 225°–230° | 0 to 9.6 |
| 230°–235° | 0 to 6.2 |
| Residue, | 4.2 to 17.4 |

Peppermint oil adulterated with light camphor oil will be found to give abnormally large fractions between 200° and 205°. Parry and Bennett (*Chem. and Drug.*, 1903, **63**, 154) isolated from many samples of adulterated oils a high boiling fraction (258° to 268°) consisting mainly of cadinene, and decided that the adulterant was African copaiba oil. Such an addition lowers the rotatory power (or the sample may even be dextrorotatory), raises the refractive index, and of course lowers the menthol content.

Another adulterant of oil of peppermint, identified by Bennett (*Chem. and Drug.*, 1903, **62**, 591) is purified "acetin," a mixture of the 3 (mono-, di-, and tri-) propenyl acetates, which was present to the extent of about 15%. The adulterant was obtained in the residue after distillation under reduced pressure. This residue was optically inactive, and had a sp. gr. of 1.166 and a ref. index of 1.4355. A

sample of the mixed acetins prepared by Bennett had a sp. gr. of 1.187 and a ref. index of 1.4442. Pure oil of peppermint gives no fraction having a higher sp. gr. than about 0.960, nor ref. index much outside the limits 1.461 to 1.479. Oils containing triacetin do not respond to the alcohol solubility test, since, although soluble at first, on addition of more 70% alcohol oily drops separate on standing.

Parry and Bennett also detected (*Chem. and Drug.*, 1904, **64**, 854) adulteration of peppermint oil with cedar-wood oil. Three samples showed a sp. gr. of 0.908, an opt. rot. of −24°, a refractive index of 1.4670 at 20°, and a total menthol content of 48 to 49%. The oils were insoluble in 70% alcohol, from 30 to 50% floating on the surface of the liquid. Fractional distillation revealed the presence of cedar-wood oil by the increasing sp. gr., optical rotation, and index of refraction of the later portions of the oil. By refractionation of the last 5% distilled, Parry and Bennett obtained fractions showing sp. gr. ranging from 0.914 to 0.933; opt. rot. −40° to −45°, and ref. index, 1.470 to 1.500. Some of these fractions had a distinct cedar-wood taste.

African copaiba oil, which is also used as an adulterant, alters the physical characters in the same manner as does cedar-wood oil.

Schimmel & Co. (*Report*, 1919) have found phthalic ester as adulterant to the extent of 65%. The adulterated oil was conspicuous on account of its high sp. gr., its low opt. rot. and abnormal ester value. Another adulterant reported by the same firm is glyceryl acetate.

Marshall and Salamon (*Perf.* and *Ess. Oil Record*, 1922, **13**, 4, 105) report on an ingeniously sophisticated French peppermint oil. The supposed French oil consisted of a dementholised rectified Japanese peppermint oil plus castor oil and alcohol. The physical and chemical characters of the oil were within the range of figures usually ascribed to French oil of peppermint.

Several colour tests of peppermint oil have been described, but these are of little use as tests of purity. The best known is that produced by glacial acetic acid with English and American oils. Japanese oil does not respond. When about 5 drops of the oil are mixed with 1 c.c. of glacial acetic acid, a blue is obtained (after several hours), which gradually increases in intensity up to 24 hours. With American peppermint oil a dark blue is seen when viewed by transmitted light, and a fine copper-coloured fluorescence with reflected light. The English oil gives a similar though less pronounced

CHARACTERS OF NORMAL PEPPERMINT OILS

| | American | English (Mitcham) | French | Italian | German | Russian | Chinese | Japanese |
|---|---|---|---|---|---|---|---|---|
| Botanical origin... | M. piperita | M. piperita | M. piperita | M. piperita | M. piperita | M. piperita(? | M. canadensis var. glabrata(?) | M. arvensis |
| Sp. gr. ........... | .895 to .915 | .900 to .912 | .910 to .930 | .905 to .926 | .898 to .915 | .903 to .920) | 0.909 to .918 | .896 to .906 |
| Opt. rot. ........... | $-18°$ to $-35°$ | $-23°$ to $-32°$ | $-5°$ to $-35°$ | $-2°$ to $-27°$ | $-23°$ to $-27°$ | $-15°$ to $-26°$ | $-35°$ to $-45°$ | $-29°$ to $-42°$ |
| Ref. ind. ........... | 1.460 to 1.464 | 1.4600 to 1.4640 | 1.461 to 1.471 | 1.4615 to 1.4680 | 1.4580 to 1.4685 | ........... | ........... | 1.460 to 1.462 |
| % combined menthol... | 5 to 14 | 3 to 21 | 4 to 20 | 3 to 11 | 2.8 to 20.8 | 3 to 10 | 8 to 16 | 63 to 84 |
| % free menthol... | 43 to 51 | 47 to 49 | 41 to 50 | 41 to 56 | 45 to 60 | 47 to 50 | 56 to 62 | 3 to 6 |
| % total menthol... | 48 to 65 | 50 to 70 | 45 to 70 | 44 to 67 | 48 to 81 | 50 to 60 | 64 to 78 | 70 to 90 |
| Solubility 70% alcohol... | 2 to 5 | 3 to 4 | 4[1] | 3 | 2.5 to 5 | ........... | 2.5 | 2 to 3 |

[1] Some normal oils are not soluble in 70% alc.

result.   Slight warming of the mixed liquid accelerates the action, a violet-blue resulting.   The effect is due to oxidation, since it only takes place in presence of air.   Oils previously exposed for some time to sunlight do not give the colour.   (See further P. Welmans, *Pharm. Zeit.*, 1901, **46**, 591.)

The reaction may be very quickly produced by operating in the manner described in the U. S. P. (1890); 2 c.c. of the oil are mixed with 1 c.c. of glacial acetic acid and 1 drop of nitric acid.   Under these conditions even Japanese oil gives a slight violet.

Umney (*Perf. and Ess. Oil Record*, 1911, **2**, 275) gives the following colour reaction to distinguish Japanese from other peppermint oils:

1 c.c. of the oil is heated with 0.5 grm. of a mixture of equal parts paraformaldehyde and citric acid over a water-bath.   With Japanese peppermint oil there is no coloration, whereas with American, English, Italian and German oils, a purple colour develops.   This new test has the advantage of being quicker than the familiar colour test with concentrated acetic acid.

*Spirit of Peppermint* and essence of peppermint, for which the pharmacopœial preparation is generally supplied, is a solution of 1 part by measure of peppermint oil in 9 parts of 90% alcohol.

Peppermint oil is a source of menthol and is used widely as a flavouring for confectionery, cordials, dentrifices, etc.   It is used medicinally as a carminative.

### Spearmint Oil

The British Pharmacopœia describes this oil as being obtained by distillation from the fresh flowering spearmint, *Mentha viridis*. American oil is obtained from *M. spicata*, whilst the German oil is obtained from *M. crispa*.   The botanical source of Russian spearmint oil is doubtful.

Spearmint oil is colourless, pale yellow, or greenish-yellow when recently distilled, becoming darker with age.   It has the odour and taste of the herb.   The B. P. states that the oil has a sp. gr. of 0.925 to 0.940, opt. rot. $-30°$ to $-50°$; and is soluble in 3 parts of 90% alcohol.

With 80% alcohol the oil forms a clear solution in equal volumes, but turbidity is produced on further dilution with the alcohol (United States Pharmacopœia, (9th Rev.).

The U. S. P. directs that the oil must have a sp. gr. from 0.917 to 0.934; an opt. rot. $-38°$ to $-55°$, and that it must contain not less than 43% by volume of carvone when assayed according to the method as given under caraway oil.

The following table shows the characters of several oils of this class, based mainly on the results of Schimmel & Co. Only the first 2 are of practical importance:

| Geographic source | Botanical source | Sp. gr. | Opt. rot. | Ref. ind. | Solubility | Carvone, % |
|---|---|---|---|---|---|---|
| America................ | M. spicata | 0.920 to 0.940 | $-35°$ to $-53°$ | 1.480 1.489 | 1 to 1.5 vols. 80 % alc. | 33 to 66 |
| Germany................ | M. spicata | 0.920 to 0.940 | $-34°$ to $-52°$ | 1.482 1.489 | 1 to 1.5 vols. 80 % alc. | 42 to 60 |
| England............... | M. viridis | 0.926 to 0.935 | $-39°$ to $-52°$ | ....... | 1 vol. of 90 % alc. | 30 to 48 |
| Austria................ | ............ | 0.936 to 0.952 | $-38°$ to $-50°$ | 1.489 to 1.493 | 1 vol. and more 80 % alc. | 61 to 72 |
| Russia................. | M. verticillata | 0.880 to 0.890 | $-20°$ to $-28°$ | ....... | ............ | 5 to 10 |

Oil of spearmint contains lævopinene, lævolimonene, carvone, and probably small amounts of linalol and other substances.

Nelson (*U. S. Dept. Agr. Bur. Chem. Cir.*, 92) has identified phellandrene as a constituent of this oil. Dihydrocumic acetate has been found in German spearmint oil by Elze (*Chem. Zeit.*, 1910, **34,** 1175), and Nelson (*loc. cit.*) has found dihydrocarveol acetate in American oil. The proportion of carvone ranges from about 35 to 55%. It may be estimated as described on page 567. Russian oils appear to contain cineole.

Schimmel & Co. have described a spearmint oil (distilled by them in America) which had a sp. gr. of 0.980 and an optical rotation of $-42.5°$. It appeared to contain an abnormally large amount of carvone.

Irk (*Pharm. Central*, 1911, **52,** 1111) has examined Hungarian spearmint oil which had the following characters:

Sp. gr. 15°/4°............................ = 0.9375 to 0.9513
Optical rotation......................... = $-44.4°$ to $-49.9°$
Ref. index............................... = 1.4899 to 1.4931
Carvone.................................. 62–71%

It is soluble in its own volume of 80% alcohol.

Spearmint oil is used principally as a flavouring agent in chewing gum and confections.   It is also used medicinally.

## Pennyroyal Oils

True pennyroyal oil is from the herb of *Mentha pulegium;* American oil from the herb of *Hedeoma pulegioides.*

The true oil is yellow or reddish-yellow with a strong odour.   The sp. gr. is usually within the limits 0.930 to 0.960, but Umney and Bennett (*Pharm. J.,* [4], 1905, **21,** 860) reported a sample of Silician origin with a sp. gr. 0.927 at 15° and an optical rotation of +35.   The usual optical rotation is from +17 to +23.   The refractive index is about 1.4800 (Parry).

The oil is soluble in 2 or more volumes of 70% alcohol.

Pennyroyal oil contains menthol, pulegone, α- or β-isopulegone (possibly), menthone, and terpenes (probably lævolimonene and dipentene).   About 80% of the oil distils between 212° and 216°. Adulteration with turpentine oil lowers the sp. gr. and b. p. of penny-royal oil, while it is less soluble in alcohol when this adulterant is present.

A Russian oil derived from *Pulegium micranthum* has a sp. gr. of about 0.930.

The composition of American pennyroyal oil has been closely studied by Barrowcliff (*J. Chem. Soc.,* 1907, **91,** 875), who found the principal constituents to be lævomenthone and dextro-isomenthone (together, about 50%); pulegone, about 30%; 1-methyl-3-cyclo-hexanone, 8%; with lævopinene, lævolimonene, and dipentene in small proportions.   A sesquiterpene alcohol was present in a propor-tion of about 2%, and a small proportion of methyl salicylate.

The oil examined had a sp. gr. of 0.9297 at 15°/15°, an opt. rot. of 25.73°, and was soluble in twice its volume of 70% alcohol.

Schimmel & Co. give 0.925 to 0.940 as the limits of sp. gr.

The solubility of the oil in 2 or more volumes of 70% alcohol enables the detection of petroleum, turpentine, and resin oil as recorded by E. Kremers (*Proc. Am. Phar. Assn.,* 1902, **50,** 979).

Schimmel and Co. (*Report,* Nov., 1908) report as an adulterant, eucalyptus oil which was discovered by the low pulegone content of the suspected sample.   Cineole was separated from the suspected sample.

Pennyroyal oil is used medicinally and as a source of pulegone.

## Pimento Oil (Allspice Oil)

This oil is obtained by the distillation of the dried unripe fruit of *Pimenta officinalis*. It is yellow or yellowish-red becoming gradually darker. It has the odour and taste of pimento, which resembles a mixture of cinnamon, nutmeg, pepper, and cloves, the last mentioned predominating. Hence the name "allspice."

The U. S. P. (9th rev.) requires for pimento oil a sp. gr. of 1.018 to 1.048 at 25°, an opt. rot. 0° to −4°, and that the oil should be soluble in an equal volume of 90% alcohol, also soluble in 2 vols. of 70% alcohol. It is also required to contain not less than 65% of eugenol, when assayed by Umney's process. (See page 501.)

Schimmel & Co. give the limits of sp. gr. of this oil as 1.024 to 1.050, and state that the B. P. limits require correction. According to the experience of English chemists, however, it seems improbable that an oil of 1.024 sp. gr. contains a due proportion of eugenol.

Pimento oil consists for the most part of eugenol, which is present to the extent of about 65 to 70 (or even 80)%. In addition, the oil contains cineole, lævophellandrene, methyl-eugenol, caryophyllene, and palmitic acid. The oil closely resembles oil of cloves in composition and properties.

The sp. gr. of genuine oil of pimento usually ranges from 1.024 to 1.055. The optical rotation ranges from −1° to −5°, ref. ind. at 20°, 1.525 to 1.534, soluble in 1 to 2 vols. and more of 70% alcohol, and contains from 65% to 80% of phenols.

Fractional distillation is a valuable aid in judging of the purity of this oil. The sp. gr. is higher according as the eugenol content is higher, and the fraction distilling over between about 245° and 250° should be large, as it contains the whole of the eugenol, b. p. 247°. The proportion of eugenol, as estimated by Thoms' method (page 502), should be at least 60 to 65%.

Oil of pimento leaves is described (*Bull. Imp. Inst.*, 1913, **11,** 438) as having a sp. gr. 1.026 at 15°, and an opt. rot. of −5.5°. It was soluble in 1.6 vols. of 70% alcohol and contained 68% phenols principally eugenol.

Pimento oil is employed as a flavouring agent for various medicinal preparations.

## Pine-needle Oils

Under the above title are comprised the volatile oils of the needles and young shoots of many coniferous plants. They are colourless

## CHARACTERS OF PINE-NEEDLE OILS

| | Sp. gr., 15.5° | Opt. rot., ° | Solubility in alcohol (90%) | Esters as bornyl acetate, % | Behaviour on distillation | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | First distillate at | 150 to 170°, % | 170 to 185°, % | Residue, % |
| **Genuine Pine Oil.** 1. From needles and twigs of *Picea vulgaris* (Norwegian spruce). | 0.880 to 0.888 | −21.7 to −37 | ...... | 8.3 to 9.8 | 160° | 20 | 50 | 30 |
| 2. From needles and twigs of *Abies alba* (Miller) (*Abies pectinata*; silver fir). | 0.869 to 0.875 0.885 | −20 to −59 −35 | 1:5 1:6.5 | 4.5 to 11 6.1 | 162° | 8 | 55 55 (Limonene.) | 37 ...... |
| 3. From cones of *Abies alba* (Miller) (fir-cone oil). | 0.853 to 0.870 | −60 to −84 | 1:6 | 0.5 to 6 | ...... | 11 | 37 (Limonene.) | 52 |
| 4. From twigs of *Abies alba* (*A. pectinata*). | 0.854 | −72.4 | ...... | (No borneol.) | ...... | 16 | 76 | 8 |
| 5. Needles and young twigs of *Pinus pumilio* (Haenke) *Pinus Montana*). | 0.865 to 0.875 | −4.5 to −9 | 1:8 | 5 to 8 | 170° | ...... | 70 (to 180) | 30 |
| 6. Needles of *Pinus sylvestris* (English). | 0.885 to 0.889 | −7.7 to −19 | ...... | 2.9 to 3.5 | ...... | 8 to 13 | 33 to 47 | ...... |
| 7. Needles of *Pinus sylvestris* (German). | 0.865 to 0.886 | +5 to +10 | 1:10 | 1.0 to 3.5 | 160° | 10 | 46 | 44 |
| 8. Needles of *Pinus sylvestris* (Swedish). | 0.872 | +10.7 | ...... | 3.5 | 160° | 44 | 40 | 16 |
| 9. Needles of *Pinus cembra* (Siberian Cedar). | 0.865 | +29.1 | ...... | ...... | ...... | ...... | ...... | ...... |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 10. Needles and twigs of *Abies Siberica* (Siberian (*Larix Siberica*). | 0.905 to 0.925 | −37 to −43 | 1:1 | 29–40 | | | | |
| 11. Needles of *Picea nigra* (black spruce). | 0.922 (20°) | −36.4 | | 48.8 | | 11 | 37 | 52 |
| 12. Needles and young twigs of *Abies Canadensis* (hemlock); *Picea alba* (white spruce; and *Picea nigra* (mixed distillate) [hemlock or spruce oil]. | 0.907 to 0.913 | −21 to −24 | | 36 | | | | |
| 13. Fresh twigs and young cones of *Balsam fir.* (North America). | 0.888 (20°) | −28.9 | | 17.6 | | 49 | 29 | 22 |
| 14. Needles of *Larix decidua* (Larch). | 0.878 | +0.7 | 1:5 | 8.1 | | 54 | 24 (to 190°) | |
| Factitious Oil. | | | | | | | | |
| A. | 0.873 | +14 | | | | 96 | 1 | 3 |
| B. | 0.868 | +4 | | | | 95 | 1 | 4 |
| C. | | Inactive | | | | 100 | | |

(Chiefly at 212° to 230°.)

liquids of balsamic odour. In composition they are in a strongly marked contrast to the different forms of turpentine oil, yielding only a small percentage of distillate below 170°. A characteristic constituent of pine-needle oils is bornyl acetate, though other esters of borneol may be present in some varieties. Pine-needle oils contain several terpenes, mostly lævorotatory, among which lævo- and dextropinene, lævolimonene, dipentene, phellandrene and sylvestrene have been recognized. The table on pages (112 and 113) shows the characters of the chief pine-needle oils, the data being taken from the researches of Bertram and Walbaum (Schimmel & Co., *Rep.*, Oct., 1892; *Arch. Pharm.*, 1893, **231**, 290) and from the results of Gildemeister and Hoffmann (*The Volatile Oils*). The characters of certain factitious oils examined by the first-named observers are also included in the table.

From the figures it appears that pure pine-needle oil yields on distillation only a moderate fraction below 170°, and leaves a considerable portion undistilled at 185°. This residue consists chiefly of bornyl acetate with other esters of borneol.

Sample 4, a pine-twig oil from *Abies excelsa* or *pectinata*, contained no appreciable quantity of borneol or its derivatives (0.5%), the oil consisting almost entirely of lævopinene and lævolimonene, which latter constituent was recognised by the m. p. of the hydrobromide (104°).

The so-called American hemlock or spruce oil (12) contained 36% of bornyl acetate, the other constituents being lævopinene and a sesquiterpene (cadinene).

Pumilio oil (pine oil) contains smaller proportions of pinene and borneol derivatives, but the presence of phellandrene is indicated by the ready formation of its nitrite. Sylvestrene and cadinene are also present. In the Austrian Alps, the needles and branches of *P. pumilio* are distilled on a large scale, and the oil obtained is used extensively in soap-making and perfumery. A sample of 0.865 sp. gr., and −9° rotation contained lævopinene and lævophellandrene, sylvestrene, bornyl acetate (5%), and cadinene. The oil produced in Sweden from the needles of *P. sylvestris* (No. 8 in table) contained dextropinene, sylvestrene, and probably some bornyl acetate. The German oil from the same tree had a similar composition.

According to the United States Pharmacopœia, (9th rev.), pine needle oil is distilled from the fresh leaves of *Pinus montana*, and it

should have a sp. gr. of 0.853 to 0.869 at 25°, and no portion distilling under 170°.

Bertram and Walbaum state that pinene is generally present in pine-needle oil, but that while the oils from *Abies picea* contain chiefly lævopinene, the product of the ordinary fir contains the dextro modification.

According to Tröger and Bentin (*Arch. Pharm.*, 1904, **242,** 521), the oils distilled from the young shoots of *P. sylvestris* and *P. strobus* contain dextro- and lævopinene, respectively, but are free from sylvestrene, cadinene, and the borneol esters present in the oils from older leaves, which compounds are thus produced in later growth.

Of the *factitious pine oils* represented in the table, A and B consisted substantially of ordinary turpentine oil with a small addition of true pine-needle oil, while C contained ethyl acetate, which distilled as a first running below 150°.

In a fraction of Siberian pine-needle oil, b. p. 240° to 280°, Wallach and Grosse (*Ann.*, 1909, **368,** 19) found a sesquiterpene which readily yielded a crystallisable hydrochloride.

Bocker and Hahn (*J. prakt. Chem.*, 1911, **11,** 83, 489) isolated a new *aldehyde*, $C_{15}H_{22}O$, a new *ketone*, $C_{15}H_{24}O$, and a third compound, $C_8H_{14}O$, which has been named *pumilone*, from the oil of *Pinus pumilio*.

A. W. Shorger (*J. Ind. Eng. Chem.*, 191, **6,** 723, 809, 893, 1915, **7,** 24) has distilled and examined numerous authentic samples of pine needle oils from various botanical sources and various geographic localities.

Pine needle oil is extensively used in medicinal preparations and also in scenting soaps, in disinfecting agents, etc.

### Rose Oil (Otto of Roses; Attar of Roses)

This essential oil, so important to the perfumer, is obtained from the fresh flowers of *Rosa Damascena*, *R. centifolia*, *R. alba*, and other varieties and is chiefly distilled in Bulgaria. The oil is very liable to adulteration, and both the Bulgarian distillers and the Turkish dealers sometimes add palmarosa oil (Turkish geranium) and other products. An examination of the "odour" of rose otto is still one of the best guides to purity.

Rose oil deposits at ordinary temperatures a variable amount of stearoptene as a crystalline mass. The white rose yields a somewhat

larger quantity of stearoptene than the red rose. At temperatures slightly higher (30°), rose oil is a pale yellow fluid. Its sp. gr. at 15.5° is 0.860 to 0.870, and about 0.848 to 0.858 at 30° (rarely above 0.856). The British Pharmacopœia (1914) states that rose oil (which according to that authority should be distilled from *R. Damascena*) has a sp. gr. of 0.854 to 0.862 at 30°, and congeals and melts at from 20° to 23°. These requirements are misleading and inadequate. The congealing and m. p. of the oil differ according to the proportion of stearoptene present.

Rose oil is only slightly optically active, the mean rotation being about $-3°$. Some few German oils are faintly dextrorotatory ($+1°$).

Citronellol from oil of roses is, however, lævorotatory to the extent of $-4.3°$.

According to Parry (*Chemistry of the Essential Oils*, 2d Ed.), the ref. index is a valuable datum, and should fall within the limits 1.4580 and 1.4650. Geraniol raises this figure perceptibly, so does palmarosa oil, which has a ref. index of 1.4745. Alcohol has ref. index 1.365.

The *constituents of rose* oil have been the subject of much study. It has been known for many years that rose oil and oils of the geranium variety contain an alcohol, $C_{10}H_{18}O$, to which Jacobsen, in 1870, gave the name "geraniol." Bertram and Gildemeister then recognised that rose oil contained a mixture of 2 alcohols, of which geraniol, $C_{10}H_{18}O$, was the chief. Tiemann and Schmidt finally proved the identity of the other alcohol with that obtained by Dodge in 1890 by reduction of citronell-aldehyde. This alcohol is citronellol, $C_{10}H_{20}O$. Much confusion has arisen on account of the numerous names which have been given by the various workers on the subject to one or other of these 2 alcohols. Many of these names have now been abandoned, as most of the products have been found to consist of geraniol and citronellol in varying proportions. Thus the "rhodinol" of Erdmann and Huth, and the "lemonol" of Barbier and Bouveault consist of geraniol; the "rhodinol" of Eckart, the "roseol" of Marknovnikoff and Reformatsky, and the "réuniol" of Hesse are mixtures of geraniol and citronellol; whilst the "rhodinol" of Barbier and Bouveault and the "réuniol" of Naschold are identical with citronellol. Substances sold in commerce under the names of "rhodinol" and "réuniol" are mixtures of geraniol and citronellol.

Commercial "rhodinol" consists of a mixture of 30 to 40% of citronellol and 60 to 70% of geraniol. "Licarhodol" was the name given by Barbier to a product obtained by heating linalol with acetic anhydride. According to Schimmel & Co., it consists of geraniol and dextroterpineol.

The principal constituents of both Bulgarian and German oil of roses are, therefore, the alcohols geraniol and citronellol. These alcohols are present in the oil in the proportion of 75% of geraniol to 25% of citronellol. German oils, however, contain less citronellol than Bulgarian oils.

The presence of geraniol in oil of roses (and also in African geranium oil) may be shown by treating the liquid portion of the oil with calcium chloride, when the characteristic crystalline geraniol and calcium chloride compound is produced. Citronellol does not form a corresponding compound. Another method of detecting the presence of geraniol in essential oils is to isolate the diphenylurethane derivative which crystallises in colourless needles, m. p. 82°. Citronellol diphenylurethane is an oily, non-volatile compound. Citronellol is estimated in rose oil by formylating a mixture of 1 volume of oil with 2 vols. of 100% formic acid, heating for 1 hour over a reflux condenser. The method is then conducted as in the acetylation of oils (page 593). Other processes for the detection and estimation of the open-chain alcohols in rose oil, are described in detail on page 593 *et seq.*

In addition to the 2 chief alcoholic constituents and the stearoptene, already described, other substances occur that, although in small quantity, appreciably modify the odour. Among these are traces of esters of geraniol and citronellol, together with acids produced by slight decomposition. According to some observers an easily hydrolysed lævorotatory ester is present in the oil, and to the decomposition of this is ascribed the acidity of rose-flower water. Walbaum and Stephan have proved the presence of normal nonyl aldehyde, citral, and linalol. Schimmel & Co. prepare a synthetic "otto" based on the researches of Walbaum and Stephan. Erdmann has shown normal phenyl-ethyl alcohol to be present (partly as esters) and, according to Eckart, ethyl alcohl (5% of the liquid portion) is a normal constituent of the oil, but this is only present in the product from roses which have partly fermented before distillation (Poleck). Von Soden and Treff claim to have isolated

nerol (5 to 10%), eugenol (1%), and a sesquiterpene alcohol ("farnesol"?), 1%.   Phenyl-ethyl alcohol is especially important as contributing to the odour of rose otto, but, although this compound is present to a considerable extent in rose-flowers, it only occurs in small amount in rose otto, being largely lost in the distillation-water.

The *stearoptene* present in rose oil is apparently a mixture of 2 solid hydrocarbons, m. p. 22° and 41°, respectively.   The mixed substance, as it exists in the oil, melts at 33° to 35°.   The proportion of stearoptene present in different oils varies within very wide limits, so that the amount of this constituent is no criterion as to the purity of the oil.   According to E. J. Parry, Bulgarian oils contain 10 to 20% of stearoptene, while the oils from France, Germany, and England are said to contain 25 to 60%.   Any oil containing a percentage of stearoptene, even approaching this higher figure, cannot be regarded as a normal product.

The *sp. gr.* of rose oil ranges between fairly wide limits and according to the proportion of stearoptene.   Adulteration of rose otto with alcohol causes a low sp. gr.

The *congealing-point* (setting-point) of rose otto may be ascertained, in the following manner (P. N. Raikow, *Chem, Zeit.*, 1898, **22,** 149): About 10 c.c. of the oil to be examined is placed in a test-tube of 15 mm. diameter, and the oil warmed by means of the hand until it attains a temperature well above the solidifying-point.   A thermometer is meanwhile placed in the oil in such a manner that it touches neither the bottom nor the sides of the tube, but has its bulb completely immersed.   The oil is allowed to cool spontaneously, and the temperature at which the first crystals appear is the congealing-point.   Duplicate determinations should be made.

Adulterated rose oil may contain paraffin wax or spermaceti, which should be looked for in the separated solid portion of the oil. The stearoptene of rose oil usually melts at 33° to 34°, and should not exceed the limits of 32° to 37°.   Higher m. p. indicates adulteration with paraffin wax or spermaceti.

Parry states (*Chemistry of Essential Oils*) that, while the detection of spermaceti and stearin in rose oil is comparatively easy, the detection of paraffin wax or the solid constituent of "guaiacum-wood" oil presents greater difficulty.   On saponifying the stearoptene of the oil under examination, no fatty acids will be obtained if the oil is pure, while spermaceti and stearin yield palmitic and stearic

acids (m. p. at 55°–62° and 62°–68°, respectively). Paraffin wax may be detected by its more granular crystalline structure as compared with the rose stearoptene. The alcoholic body from guaiacum-wood oil will yield an acetyl value. Antipyrin is occasionally found as an adulterant of rose-otto.

According to E. P. Paetzold, the so-called concrete oil of guaiacum wood is the product of *Bulnesia sarmienti*, and is one of the chief adulterants of Turkish rose oil. It is used especially in conjunction with geranium oil. It has a mild tea-like odour, and consists largely of a crystalline alcohol of m. p. 91°, and is thus semi-solid at the ordinary temperature. The oil is stated to have a sp. gr. of 0.969 at 35° and an opt. rot. of −6.7°.

The following figures show the physical characters of different varieties or rose oil, as recorded by various observers:

| Variety of rose oil | Sp. gr. | Opt. rot. | Solidifying point | Total alcohols, % | Stearoptene, % |
|---|---|---|---|---|---|
| Bulgarian............ | 0.849 to 0.858 (30°) | −1.5° to −4° | 19° to 22° | 68 to 78 | 15 to 20 |
| Bulgarian............ | 0.849 to 0.862 (30°) | −1° to −4° | 18° to 23.5° | 66 to 75 | 17 to 21 |
| French.............. | 0.8225 to 0.8407 (30°) | −6.95° to −8° | ............ | ........ | 26 to 35 |
| French.............. | 0.859 to 0.874 (30°) | −2° to −4° | 19° to 28° | 70 to 78 | 26 to 35 |
| German............. | 0.838 to 0.850 (30°) | +1° to −1° | 29° to 31° | 70 to 80 | 26 to 40 |
| German............. | 0.836 to 0.844 | −0.75° to −1° | 29° to 30° | 54 to 60 | 28 to 40 |
| Russian............. | 0.8368 | −4.25° | 23° | 50 | 33.5 |
| Spanish............. | 0.825 to 0.845 | −1° to −3° | 25° to 29° | 45 | 33 to 50 |

Parry (*Chem. and Drug.*, 1909, **75**, 186) examined four authentic samples of the crop of 1909 and found the following range of constants:

Sp. gr. 30°, 0.8568 to 0.8573;

Opt. rot. −2° 30′ to −3°;

Ref. ind. 25° 1.4626 to 1.4730.

After washing the oil with water the ref. ind. was 1.4630 to 1.4638; m. p., 22.5°. Total geraniol, 68.5 to 71%.

The following notes will afford some information in regard to ottos of rose other than Bulgarian, which are now to be found on the market.

**Anatolian Otto.**—This otto may have a high m. p. varying from 19° to 26°, and a sp. gr. up to 0.8635. The following represent typical samples, the figures varying according to the stearoptene content:

| | | | | |
|---|---|---|---|---|
| Sp. gr. 30°/15°.......... | 0.863 | | Sp. gr. 30°/15°.......... | 0.850 |
| Optical rotation......... | −2° 30′ | | Optical rotation......... | −3° |
| Ref. index at 25°......... | 1.4650 | | Ref. index at 25°......... | 1.4600 |
| Ref. index, after washing. | 1.4652 | | M. p................... | 23° to 24° |
| M. p................... | 21° to 22° | | Citronellol.............. | 41.1% |
| Stearoptene content...... | 15.8 | | Total alcohols........... | 66.8% |
| Total alcohol, calculated | | | Stearoptene............. | 18.9% |
|   as geraniol............ | 72.8% | | | |
| Citronellol.............. | 36.2% | | | |

**French Otto.**—This otto has become a commercial article. Very few authentic samples have been examined, but it appears to have characters which differ within wide limits, and it must, at present, be very largely judged by its odour. The sp. gr. of apparently genuine samples has been found up to 0.872, and, when distilled from white roses, down to 0.811, on account of the presence of up to 85% of stearoptene. The latter type of otto is, of course, of little value from the point of view of odour. Umney has examined a Spanish distillate and finds it to have the following characters:

| | |
|---|---|
| Sp. gr. 30°/15°.................................. | 0.844 |
| Opt. rot....................................... | −2 |
| Ref. ind....................................... | 1.4565 |
| M. p.......................................... | 27° to 28° |
| Percentage of stearoptene........................ | 33.3 |
| M. p. of separated stearoptene.................... | 31–32° |

The sp. gr. of rose oil is not of much value when considered apart from other constants, since the several varieties of the oil differ to a not inconsiderable extent, and the content of stearoptene also causes differences. According to J. C. Umney, a rose oil having a sp. gr. exceeding 0.861 at 30° should be looked upon with suspicion. The figures for the opt. rot. of rose oil and its adulterants do not show sufficiently well-marked differences to be valuable in ascertaining the purity of rose oils.

The m. p. and solidifying points of genuine rose oils may be taken as lying between the limits 17° and 23°, although the percentage of stearoptene affects them. A high solidifying point indicates excess of stearoptene (or adulteration with paraffin wax), while the odour of the oil will be correspondingly weakened. Oils adulterated with geranium oil have a lowered solidifying point and of course contain a decreased proportion of stearoptene. For the estimation of the amount of stearoptene present in the oil, Schimmel & Co.

(*Rep.*, 1889) advise heating 50 grm. of the sample with 500 grm. of 75% alcohol to 70° to 80°.   On cooling the mixture to 0° the stearoptene separates almost quantitatively.   The liquid is filtered, again treated similarly with 200 grm. of the alcohol, and this treatment is continued until the stearoptene is quite odourless.   Two treatments of the crude stearoptene are usually sufficient, and the product is then dried and weighed.

According to F. Dietze, the acid and ester values of pure rose oils (in terms of % potassium hydroxide) range from 0.12 to 0.26 (acid value) and from 0.65 to 1.9 (ester value), while geranium oils show an ester value of 2. 60 7.2.   These constants are of very doubtful value as an indication of purity (see P. N. Raikow, *Chem. Zeit.*, 1898, **22,** 149).

The estimation of the relative proportions of geraniol and citronellol in otto of rose is now recognised as one of the principal analytical factors in the examination of the oil.   The amount of citronellol present varies with the country of origin of the sample.   In Bulgarian otto of rose it is usually about 30–33%, and any sample falling below 28% should be regarded with considerable suspicion.

The adulteration with geraniol, if the adulterant be derived from palmarosa oil, is sometimes indicated by the presence of gurjun balsam oil, which has been used as an adulterant of the palmarosa oil. Much gurjun oil is indicated by a high lævorotation, and samples with this value in excess of $-4°$ should be carefully examined.   As little as 0.5 to 1% of gurjun oil may be detected by adding 5 or 6 drops of the sample to 10 c.c. of acetic anhydride containing 5 or 6 drops of nitric acid.   A distinct purple colour develops if gurjun oil be present, the depth depending on the amount of the adulterant.

In the examination of otto of rose it must be remembered that the characters vary from season to season, and there is, in the writer's opinion, no essential oil more difficult to judge than this one.   An expert nose will often yield as much or more information than the analytical values.

Umney found the finest ottos to contain 71 to 72.5% of total alcohols.   High stearoptene-content lowers this figure, while admixture with geranium oil raises it considerably, and at the same time increases the sp. gr.   Umney cites the following results (among others) obtained by the examination of the genuine and adulterated samples of rose oils:

|  | Genuine oils | | | Adulterated samples | | |
|---|---|---|---|---|---|---|
|  | 1 | 2 | 3 | 4 | 5 | 0 |
| Sp. gr., 30°..................... | 0.875 | 0.860 | 0.861 | 0.863 | 0.868 | 0.868 |
| Crystallising-point............. | 20.9 | 20.4 | 20.0 | 19.4 | 18.7 | 18.9 |
| Stearoptene, %................ | 18 | 16 | 14 | 12.5 | 10 | 10 |
| Alcohols (as $C_{10}H_{18}O$).......... | 70.1 | 72.3 | 73.1 | 75.6 | 77.6 | 76.6 |

Hudson-Cox and Simmons (*Analyst*, 1904, **29**, 175) recommend the iodine absorption figure as a means for detecting adulteration of natural otto of rose with the synthetic product and other substances. These observers employ 0.1 to 0.2 grm. of otto, adding 10 c.c. of chloroform or alcohol (90%), and 25 c.c. of Hübl's iodine solution. The excess of iodine in the mixture is titrated in the usual manner after the liquid has been allowed to stand for 3 hours in the dark at the ordinary temperature. Considerable differences in temperature have no appreciable effects on the results. Hudson-Cox and Simmons use only Hübl's solution of full strength, and consider it convenient and advisable to keep the iodine and mercuric chloride solutions separate, and mix them the evening before using. The titration should be carried out as rapidly as possible. It is noteworthy that, while the artificial otto is almost deodorised by iodine, the natural otto is unaffected in this respect. The following results, in addition of those recorded in the table on page 123, were obtained in this manner: Palmarosa oil, 296 to 307% of iodine absorbed; geranium oils: (African), 213 to 225, (Bourbon), 213 to 215, (Spanish), 211, citronella oil, 217; guaiacum wood oil, 298; geraniol, 307 (?); citronellol, 187; linalol, 280; citral, 175; and the stearoptene of rose oil, none. With the exception of citronellol and citral, all the iodine values largely exceed those of genuine otto of rose, the oils of citronella, which most closely resemble otto of rose in this respect, being readily recognisable by their ester content.

The figures in the table (page 123) have been recorded by Hudson, Cox and Simmons and by W. H. Simmons (*Chem. and Drug.*, 1904, **65**, 707) for various samples of genuine and artificial ottos and their adulterants.

Jeancard and Satie (*Bull. Soc. Chim.*, [3], 1904, **31**, 934) found an oil distilled from the calyx, stamen, and pistil of the rose to have the following characters: Sp. gr. 0.8704 at 15.5°; optical rotation-

CHARACTERS OF GENUINE AND ARTIFICIAL ROSE OTTOS

| | Sp. gr. at 30° | Opt. rot., 30° | Sapon. value | Solidifying pt. | Iodine absorption. % | Remarks |
|---|---|---|---|---|---|---|
| Genuine ottos (5 samples)...... | 0.851 to 0.859 | −2.1 to −2.7 | 7.5 to 15.5 | 20.3 to 21.0 | 187 to 194 | .................... |
| Genuine ottos (5 samples)...... | 0.852 to 0.856 | −1.8 to −3.2 | 7.7 to 9.9 | 19.9 to 21.6 | 189 to 192 | Refractive indices, 1.4613 to 1.4646. |
| **Artificial Ottos.** | | | | | | |
| With stearoptene (2 samples)... | 0.863; 0.859 | −0.9; −0.2 | 20.5; 3.8 | 22.5; 21.9 | (221 to 254) | |
| Without stearoptene (2 samples). | 0.872; 0.866 | −1.3; −0.9 | 13.4; 5.7 | ............... | (261 to 279) | |
| **Commercial Ottos.** | | | | | | |
| No. 1...................... | 0.855 | −2.7 | 8.9 | 20.8 | 219 | Probably contained geraniol. |
| No. 3...................... | 0.855 | −2.7 | 8.1 | 19.8 | 206 | Probably contained artificial otto. |
| No. 4...................... | 0.858 | −1.4 | 10.3 | 21.3 | 234 | Chiefly artificial otto. |
| No. 6...................... | 0.843 | −0.8 | 16.1 | 18.5 | 133 | Contained much added alcohol. |
| No. 8...................... | 0.855 | −2.0 | 9.8 | 20.6 | 215 | Mixture of 1 part artificial with 2 parts of genuine otto. |

41°; solidifying-point, 8°; acid value, 6.12; ester value, 22.4; stearoptene (chiefly a substance melting at 14°) 51.1%; and citronellol (the only alcohol present), 13.6%.

Schimmel & Co. (*Rep.*, Oct., 1909, 107) report a case of adulteration of Bulgarian rose oil with both alcohol and geraniol. The only irregularity observed was in the index of refraction, but on washing the sample with water the sp. gr. at 30° was increased from 0.8606 to 0.8632, the ref. ind. from 1.4656 to 1.4667 and the congealing point from 20° to 21°.

Parry has pointed out that adulteration with alcohol may be indicated by the alteration in the characters of the oil after washing it with warm water.

The following figures show the effect of such adulteration on the washed oils.

|   | Original oil | | | Oil extracted with water | | | |
|---|---|---|---|---|---|---|---|
|   | $d^{36}$ | $n_D{}^{25}$ | M. p. | $d^{36}$ | $n_D{}^{25}$ | M. p. | Geraniol content |
| 1 | 0.8597 | 1.46318 | 19.6° | 0.8614 | 1.46628 | 18.7° | 77.4% |
| 2 | 0.8547 | 1.45111 | 20.2° | 0.8622 | 1.46615 | 17.5° | 68.1% |
| 3 | 0.8663 | 1.46565 | 26° | 0.8678 | 1.46684 | 26.5° | 77.5% |

Rose oil is used extensively in perfumery and cosmetics and, to a less extent, in confectionery and medicine.

## Rosemary Oil

This oil is distilled from the flowering tops of *Rosmarinus officinalis*. It is a pale yellow or colourless oil, having an odour of rosemary and a warm camphoraceous taste. The oil distilled from the dried leaves without admixture of stalks is the finest product, having a good odour and high borneol-content.

Oil of rosemary is official in the B. P. and U. S. P. It is described in the British Pharmacopœia (1914) as an oil of sp. gr. 0.895 to 0.920, which dissolves in 1 volume of 90% alcohol, and in 5 to 10 volumes of 80% alcohol. It should have an opt. rot. of −2° to +15°. The latter constant guards against the presence of turpentine oil (see below). The United States Pharmacopœia (10th Rev.) requires

rosemary oil to have a sp. gr. of 0.894 to 0.912 at 25° and to yield not less than 2.5% ester, calculated as bornyl-acetate and not less than 10% total borneol.

The constituents of oil of rosemary are somewhat numerous and include camphor, cineole, borneol and its esters (chiefly bornyl acetate), and traces of pinene and camphene. Haller (*C. r.*, 1889, **108**, 1308) states that both dextro- and lævo-camphor and dextro- and lævo-borneol are present in oil of rosemary.

English oil of rosemary is more valued in commerce than either the French or the so-called Italian variety. The latter is the cheapest oil. It is actually produced in certain of the Dalmatian Islands.

The sp. gr. of genuine oil of rosemary (English and foreign) varies from 0.900 to 0.918, possibly occasionally to 0.920, and sometimes as low as 0.894. The sp. gr. is altered by the addition of oil of turpentine, with which rosemary oil is sometimes adulterated. Parry regards the limits 0.896 to 0.920 as covering all genuine oils.

The optical rotation only rarely exceeds +15°, the British Pharmacopœia limit; Parry gives +1° to +12°. English oil is frequently slightly lævorotatory. Dalmatian oils usually give figures between the limits of +1° to +4°. Spike oil is sometimes added to oil of rosemary, and this adulterant does not interfere with the sp. gr. or opt. rot. It has been pointed out by Parry and Bennett that lævorotatory oils of rosemary are quite consistent with purity. These observers have found that the herb from Spanish and French sources may yield oils having either a lævorotation (−3°; −8.5°) or giving a lævorotatory first fraction (10%) on distillation (100 mm. pressure). These results are due to the lævopinene present naturally in the rosemary stems. (See *Chem. and Drug.*, 1906, **68**, 671.)

Genuine oil of rosemary should be soluble in from 0.5 to 2 vols. of 90% alcohol, and in 2 to 10 volumes of 80% alcohol. The solubility of rosemary oil in alcohol is disturbed by adulteration with turpentine oil or the higher fractions of petroleum.

Rosemary oil is occasionally adulterated with alcohol, which may be detected by fractional distillation. Genuine oils do not give more than about 15 to 20% of distillate under 170° (at the ordinary pressure). A larger amount than this indicates the pres-

ence of alcohol or turpentine oil.    The greater portion of rosemary oil distils between 175° and 200°.

The higher fractions of petroleum oil which are sometimes used as adulterants of rosemary oil may be detected by evaporating a sample of the oil upon the water-bath, a slight residue only remaining if the oil is genuine, while any petroleum oil will remain unvolatilised.

The proportions of esters and free alcohols are estimated in the usual way (page 593).    Calculated as borneol and bornyl acetate, the percentage of these constituents in genuine rosemary oils averages about 17 to 18% of alcohols, and 5 to 6% of esters.    The proportions of these constituents appear to range between fairly wide limits.    The lowest allowable limit for ester content might be placed at 1.5 (calculated as bornyl acetate), while 9% of alcohols (calculated as borneol) should be regarded as the lowest amount allowable, and probably 12% would be a fairer limit.    Many oils contain considerably more alcohols than this, as stated in the text. Umney found 3 genuine oils to contain from 11 to 15% of alcohols.

The following figures were determined by Parry and Bennett (*Chem. and Druggist*, 1906, **1**, 671) on samples distilled from plants sent to Parry, so that their authenticity is indisputable.

|  | 1 (Spanish) | 2 (French) | 3 (French) |
|---|---|---|---|
| Source.................................... | Leaves alone | Leaves and stalks | Leaves alone |
| Sp. gr. 15.5................................ | 0.917 | 0.897 | 0.914 |
| Opt. rot.................................. | +5° 30′ | −8° 30′ | −3° |
| Esters calculated as bornyl acetate........ | 3.2% | 3.0% | 3.6% |
| Total borneol............................. | 19.7% | 10.9% | 18.5% |
| Optical rotation of first 10% (100 mm.).... | −1° | −12° 30′ | −10° |

No. 1 was distilled from herb collected toward. the end of the summer and dried in the sun.    It consisted entirely of leaves which were well developed and of a fine green colour.    The yield was 0.89%.

No. 2 was distilled from stalky herb in the dried condition, collected in February.    The proportion of stalks amounted to nearly 60%.    Yield of oil 0.4%.

No. 3 was distilled from the same consignment as No. 2, but the stalks were separated and the leaves alone distilled.    They yielded 1.09% of oil, containing a high proportion of borneol.    The leaves

were somewhat discoloured, probably owing to some fermentation having taken place.

The following are the results of fractionation of the above oils:

NO. 1

| Fraction | | Sp. gr. | Rotation | Ref. index | B. p. commencing at |
|---|---|---|---|---|---|
| | % | | | | |
| 1................ | 10 | 0.884 | $-1°$ | 1.4676 | 152° |
| 2................ | 10 | 0.890 | $-1° 10'$ | 1.4680 | 156° |
| 3................ | 10 | 0.895 | $-1° 20'$ | 1.4681 | 159° |
| 4................ | 10 | 0.902 | $+1°$ | 1.4682 | 162° |
| 5................ | 10 | 0.903 | $+1° 20'$ | 1.4683 | 163° |
| 6................ | 10 | 0.911 | $+2°$ | 1.4686 | 165° |
| 7................ | 10 | 0.922 | $+2° 30'$ | 1.4700 | 169° |
| 8................ | 10 | 0.940 | $+3°$ | 1.4736 | 177° |
| Residue.......... | 20 | Partially crystallised. | | 1.4885 | 185° |

NO. 2

| Fraction | | Sp. gr. | Rotation | Ref. index |
|---|---|---|---|---|
| | % | | | |
| 1.................... | 10 | 0.874 | $-12° 30'$ | 1.4660 |
| 2.................... | 10 | 0.878 | $-13°$ | 1.4670 |
| 3.................... | 10 | 0.879 | $-13° 30'$ | 1.4670 |
| 4.................... | 10 | 0.883 | $-12° 20'$ | 1.4670 |
| 5.................... | 10 | 0.886 | $-11° 20'$ | 1.4670 |
| 6.................... | 10 | 0.891 | $-10° 30'$ | 1.4670 |
| 7.................... | 10 | 0.896 | $-8° 30'$ | 1.4678 |
| 8...:............... | 10 | 0.909 | $-5° 30'$ | 1.4702 |
| Residue.............. | 20 | .............. | .............. | 1.4859 |

NO. 3

| Fraction | | Sp. gr. | Rotation | Ref. index |
|---|---|---|---|---|
| | % | | | |
| 1.................... | 10 | 0.885 | $-10°$ | 1.4660 |
| 2.................... | 10 | 0.888 | $-10°$ | 1.4680 |
| 3.................... | 10 | 0.891 | $-9° 20'$ | 1.4685 |
| 4.................... | 10 | 0.896 | $-8° 10'$ | 1.4686 |
| 5.................... | 10 | 0.900 | $-7° 10'$ | 1.4686 |
| 6.................... | 10 | 0.909 | $-4° 50'$ | 1.4686 |
| 7.................... | 10 | 0.921 | $-1°$ | 1.4686 |
| 8.................... | 10 | 0.938 | $+2°$ | 1.4697 |
| Residue.............. | 20 | Partially crystallised........ | | .............. |

Rosemary oil is used in perfumery and in certain metal varnishes, dopes, etc. Medicinally the oil is used as an external rubefacient and antiseptic.

## Oil of Rue

The herb, *Ruta graveolens*, yields an essential oil characterised by its extremely low sp. gr. Algerian oil is distilled from *Ruta montana* (summer rue) and *Ruta bracteosa* (winter rue). The oil is of a pale yellow colour and characteristic odour, and consists almost entirely (at least 90%) of methyl-nonyl-ketone, $CH_3.CO.C_9H_{19}$, with a small amount of methyl-heptyl-ketone, except in case of R. *bracteosa* in which methyl-heptyl-ketone predominates. The sp. gr. of the oil varies from 0.830 to 0.847, and it is usually slightly dextrorotatory, from $0°$ to $+3°$. When exposed to the action of a freezing mixture the oil solidifies to a crystalline mass at $+5°$ to $+11°$. It begins to boil at $215°$, and is completely distilled at $232°$. It should dissolve to a clear solution in 2 to 3 volumes of 70% alcohol. Pure methyl-nonyl-ketone is a bluish oil, m. p. $+15°$ and b. p. $229°$. The fluorescent substance present is the methyl ester of methyl-anthranilic acid. The characters given below are sufficient to guard against adulteration, which is frequently practised, the usual adulterant being turpentine and, more rarely, petroleum, which however, alter the constants of the oil so much as to be very easily detected. Oil of rue is not largely employed in medicine, but has occasionally been employed for illegitimate purposes.

The less important constituents of this oil are pinene, limonene, cineol, and in Algerian oil, traces of methyl-salicylate. The following are the characters of the principal varieties of the oil.

| | French | Algerian (*Ruta montana*) | Algerian (*Ruta bracteosa*) | Spanish |
|---|---|---|---|---|
| Sp. gr............. | 0.830 to 0.845 | 0.830 to 0.838 | 0.837 to 0.845 | 0.833 to 0.845 |
| Rotation.......... | $-1°$ to $+3°$ | $0°$ to $+1°$ | $-1°$ to $-5°$ | $-1°$ to $+1°$ |
| Ref. ind.......... | 1.4300 to 1.4350 | 1.4300 to 1.4325 | 1.4300 | ............. |
| Solidifying point... | $5°$ to $11°$ | $+7°$ to $+10°$ | below $-5°$ | $-3°$ to $+8°$ |

The oil is used principally as a source of methyl-heptyl-ketone or methyl-nonyl-ketone. It is also used in veterinary medicine.

## Sandalwood Oil (Santalwood Oil)

There are many varieties of this oil, as several plants of the natural order *Santalaceæ* are used for its distillation. The most valuable oil, which is official in the B. P. and U. S. P., is from the East India sandalwood, *Santalum album.* The other chief commercial varieties are Macassar and West Australian. Less important are the West Indian and African oils. The East Indian and Macassar oils are derived from *Santalum album;* the Australian variety is often the product of several plants; the oil known as Swan River oil being obtained from *S. cygnorum.*

Sandalwood oil is somewhat viscid, pale yellow, with a characteristic odour and a spicy taste. The B. P. (1914) requires it to have a sp. gr. between 0.973 and 0.985, and to be soluble in 6 volumes of 70% alcohol (U. S. P., soluble in 5 vols.). This latter test ensures the absence of cedar-wood oil, and possibly other adulterants. The oil should have an optical rotation (according to the B. P.) of from $-13°$ to $-21°$. These limits of optical activity are so arranged as to exclude any other variety of oil than the product of *S. album.* The U. S. P. gives the limits of sp. gr. as 0.965 to 0.980 at 25°.

The sp. gr. of the official (East Indian) sandalwood oil is usually slightly higher than the other oils of sandalwood. Parry states that he has found genuine samples to range from 0.973 to 0.981. It has been pointed out that the sp. gr. of sandalwood oil continually increases from the commencement of the distillation to the end, so that it is necessary to take the distillation as far as possible. Thus Parry found that the sp. gr. of the oil in the first, middle, and last portions of the distillate was 0.965, 0.976, and 0.981 respectively.

Oil of sandalwood differs to an appreciable extent according to the character of the wood used in distillation. Oils from billets and roots have the finest aroma and are most used in perfumery; while oils from chips contain most santalol and are the best for pharmaceutical use.

The pharmacopœial limits for optical rotation are rarely exceeded. All genuine oils give figures between $-13°$ and $-21°$, and usually between $-17°$ and $-19°$. Most samples of genuine sandalwood oil are soluble in 4 to 4.5 parts of 70% alcohol at 20°.

Three samples of santalwood oil produced in Mauritius were found to have the following characters:

|  | Heart-wood oil | | Sap-wood oil |
|---|---|---|---|
|  | 1 | 2 | 3 |
| Sp. gr. .................... | 0.979 | 0.982 | 0.981 |
| Rotation ................... | $-20°$ 50′ | $-20°$ 55′ | $-20°$ 15′ |
| Ref. ind ................... | 1.5070 | 1.5065 | 1.5067 |
| Acid value ................. | 1.9 | 1.9 | 1.9 |
| Ester value ................ | 5.6 | 5.6 | 5.6 |
| Total santalol ............. | 96.4% | 96.4% | 95.8% |

Oil of sandalwood distils (at ordinary atmospheric pressure) between 275° and 295°, with decomposition. The results obtained by distillation under a reduced pressure of 14 mm. are much more valuable for the detection of adulteration, as the oil distils between 155° and 170°, but cedar-wood oil, a frequent adulterant, distils largely below 150° under the same conditions. According to Parry and Bennett (*Chem. and Drug.*, 1904, **64**, 202) the genuine oil (East Indian), when distilled under this reduced pressure and the distillate collected in 10% fractions, gives the following results: The sp. gr. of the fractions varies from 0.964 to 0.988; the optical rotation from $-14°$ to $-22°$; and the ref. index from 1.5038 to 1.5123 No fraction should have a ref. index below 1.5000, and the opt. rot. of the fractions should range only within narrow limits when thus distilled. The ref. index of 8 genuine samples was found by Parry and Bennett to range from 1.5040 to 1.5075 (usually about 1.5060). This figure should never be below 1.5030.

The composition of sandalwood oil has for a long time been the subject of research, since the chemistry of the alcoholic substance present (forming about 94 to 98% of the oil) was until comparatively recently in a very confused state.

The following is a complete list of the constituents of santalwood oil hitherto isolated:

*Isovaleric aldehyde*

*Santene.*—$C_9H_{14}$ (sp. gr. 0.869; rotation $-0°$ 16′).

*Nortricycloeksantalane*, $C_{11}H_{18}$ (sp. gr. 0.913; rotation $-24°$).

*Santenone.*—$C_9H_{14}O$ (m. p. 48–52°).

*Norisoborneol.*—$C_9H_{15}.OH$ (m. p. 58–62°).

*Teresantalol.*—$C_{10}H_{15}.OH$ (m. p. 112–114°).

*Nortricycloeksantalal.*—$C_{11}H_{16}O$ (sp. gr. 0.997).

*Santalone.*—$C_{11}H_{16}O$ (sp. gr. 0.991; rotation $-62°$).

*A Ketone.*—$C_{11}H_{16}O$.

*Santalene.*—$C_{15}H_{24}$ (two isomers of this sesquiterpene are present).

*α-Santalol.*—$C_{15}H_{24}O$ (sp. gr. 0.9788; rotation $+1° 13'$).

*β-Santalol.*—$C_{15}H_{24}O$ (sp. gr. 0.9728; rotation $-41° 47'$).

*Santalal.*—$C_{15}H_{22}O$.

*Teresantalic acid.*—$C_{10}H_{14}O_2$.

*Santalic Acid.*—$C_{15}H_{22}O_2$.

The acetylation process was first applied by Parry (*Pharm. J.*, [4], 1895, **1,** 118) to the examination of oil of sandalwood. It is carried out as described on page 593. Pure oils require from 0.7 to 1.5% potassium hydroxide for the saponification of the esters; but after acetylation the oil takes up 20 to 21%, owing to the presence of the large proportion of alcohols. Calculated as $C_{12}H_{26}O$, the proportion of alcoholic constituents should never fall below 90%, and a standard somewhat higher than this, say 92.5%, as suggested by Potoliet (*Brit. and Col. Drug.*, 1901, **40,** 173), would be preferable. The United States Pharmacopœia (9th Rev.), in which this method of valuation is now adopted, requires at least 90% of alcohols as "santalol." The usefulness of the acetylation method as a means of detecting adulteration may be seen from the following figures given by various oils used as adulterants, in comparison with pure sandalwood oil:

| Oil, etc. | Alcohol by acetylation (Calculated as santalol, $C_{15}H_{25}OH$), % |
|---|:---:|
| Sandalwood, East Indian............. | 92 to 98 |
| Sandalwood, West Australian.......... | about 75 |
| Cedar-wood....................... | 8 to 12 |
| Gurjun balsam..................... | 7 to 10 |
| Copaiba balsam.................... | 5 to 8 |

Harrison (*J. Assoc. Off. Agr. Chem.*, IV–425, –V, 166, 545) calls attention to the fact that it is possible to add appreciable amounts of foreign oils to sandalwood oil, and still, when assayed by the U. S. P. method, have present over 90% of alcohols calculated as santalol.

When the alcohols are calculated from the true acetyl value (obtained from the volatile acids distilled in a large-size modified Hortvet apparatus), however, this figure is materially reduced.

For details of the method reference is made to the original articles.

Thurston (*J. Am. Pharm. Assoc.*, **9**, 36) calls attention to the fact that, if sandalwood oil is adulterated with a fixed oil, the apparent santalol content is increased when assayed by the acetylation and saponification method.

He found a specimen of pure cottonseed oil gave an apparent santalol content of 96.93% by this method.

The above-mentioned adulterants, together with castor oil, are those usually found in sandalwood oil. The last-named may be identified by the lowered sp. gr. and high saponification value. Parry has recorded the adulteration of sandalwood oil with the soluble fractions of West Indian oil together with terpineol, the latter compound serving to give a fictitious santalol value. The sp. gr. of these adulterated oils was slightly low, while the opt. rot was also decreased in some cases ($-14°$). (*Chem. and Drug.*, 1906, **68**, 211.) Other adulterants of sandalwood oil are glyceryl acetate, and benzyl alcohol.

Glyceryl acetate is indicated by the high sp. gr., low rotation and high ester value, as well as by the high amount of esters which can be extracted by shaking the oil with 5% alcohol. Benzyl alcohol can be detected by fractional distillation, as it boils at about 205°. The santalol value of samples containing benzyl alcohol will usually be an impossible one—over 100%. Castor oil raises the ester value of the oil and interferes with the solubility in petroleum spirit.

The iodine absorptions of 5 samples of sandalwood oil of undoubted purity were found by Parry to vary from 190.6 to 210.3. Higher results (up to 264) were obtained by Pearmain and Moor. Similar figures are given by cedar-wood oil, and the method does not, therefore, appear to be of much value as a test of purity.

A large proportion of the sandalwood oil used in medicine is put up in the form of capsules. The oil in these capsules is frequently grossly adulterated, or is of an inferior quality. Many have been found to contain cedar-wood oil, or one of the non-official sandalwood oils (*e. g.*, West Indian). Parry has called attention to the grossly adulterated capsules on the market, many specimens consisting

largely of West Indian oil. Since it is the "santalol" of these oils which is of medicinal value, the percentage of this mixture of constituents should always be estimated. Further, it should be borne in mind that small quantities of West Indian sandalwood and cedar-wood oils (about 4% of each) may be added to East Indian sandalwood oils (see Potoliet, *Brit. and Col. Drug.*, 1901, **40,** 173) without any appreciable departure from the physical and chemical characters of genuine official sandalwood oil.

**West Australian sandalwood oil** is chiefly the product of *Santalum cygnorum*, although certain other trees are said to be employed to a small extent. The sp. gr. of this oil is lower than that of the East Indian variety, being about 0.950 to 0.965 at 15°. It is usually slightly dextrorotatory, about 5°. Parry (*Chem. and Drug.*, 1898, **53,** 708) has recorded the results of the analysis of 4 samples of this oil. They contained on the average 75.7% of "santalol" (by acetylisation). Parry believes, however, that other reactions occur during the process, and hence the above figure probably does not represent the true amount of sesquiterpene alcohols present in the oils.

In the bulletin of the Imperial Institute (1919, **17,** 109), West Australian sandalwood oil is said to be distilled from *Fusanus spicatus*. This oil is practically identical chemically and pharmacologically with oil obtained from other sources.

Owing to the presence of a small percentage of sesquiterpene the oil is not officially recognized in the B. P. and U. S. P.

The chief characters of the less important varieties of sandalwood oil are shown in the following table:

| Variety of oil | Botanical source | Sp. gr. at 15° | Opt. rot. | Constituents and characters |
|---|---|---|---|---|
| West Indian..... | *Amyris balsamifera* (*Schimmelia oleifera*) | 0.955 to 0.965 | +19° to 30° | 30 to 40 % of alcohol as "santalol," $C_{15}H_{26}O$; 16 % cadinene and other sesquiterpenes. |
| African......... | *Osyris tenuifolia*(?) | 0.948 to 0.963 | −42° to −61° | Similar to West Indian oil. |
| South Australian | *Santalum preissianum* | 1.022 | ................. | Solidifies on cooling; contains a solid alcoholic substance m. p. 101 to 102°. |
| Fiji............. | *S. yasi* | 0.9768 | −25.5° | ................. |
| Macassar........ | *S. album* | 0.974 to 0.976 | −10.6° to −16.1° | Sol. in 5 to 6 pts. 70 % alcohol; 88 to 92.5% "santalol." |

West Indian oil is characterised by its insolubility in 70% alcohol, most samples of the oil requiring over 80 parts for solution. As seen from the table, it is not a true sandalwood oil. Von Soden has isolated from this variety of oil a sesquiterpene alcohol (or mixture of isomeric alcohols), termed by him "amyrol," $C_{15}H_{26}O$. Amyrol boils at 299° to 301°, and is soluble in 3 to 3.5 parts of 70% alcohol at 20°. A compound termed *amyrolin*, $C_{24}H_{12}O_3$, is also present. (Von Soden and Rojah, *Pharm. Zeitung.*, 1900, **45**, 878.)

### Sassafras Oil

Sassafras oil, which is of great commercial importance in the United States on account of its use as a perfume in cheap toilet soaps, is obtained from the bark of the root of *Sassafras variifolium* (*S. officinale* or *S. sassafras*) a tree indigenous to North America. While the bark of the root contains the major portion of the oil, the wood contains a small amount, and the usual custom is to use the whole root.

The physical properties, as given by the United States Pharmacopœia, are as follows: "Yellow or reddish-yellow liquid, having the characteristic odour" of sassafras and a warm aromatic taste, sp. gr. 1.065 to 1.077 at 25°. The oil is dextrorotatory, but should not show more than $+4°$ at 25°. Soluble in 2 volumes of 90% alcohol, the solution being neutral to litmus-paper." The ref. index is about 1.5275. The oil contains about 80 to 90% of safrol together with small amounts of pinene, phellandrene, dextrocamphor, eugenol, and cadinene. It is being largely replaced in soap perfumery by the safrol obtained in fractionating camphor oil. The oil of sassafras leaves and stem bark is totally different from the foregoing in its physical and chemical properties.

American sassafras oil is often adulterated with camphor oil and its detection is exceedingly difficult.

### Sweet Basil Oil

This oil is distilled from the fresh herb of *Ocimum basilicum*, commercially in France, Germany, Spain and Algeria. Some oil is obtained but in smaller quantities from Java, Réunion and Mayotte.

E. G. and C. Camius (*Roure-Bertrand Fils-Bull.*, Oct., 1910) report on the botanical and chemical analysis of several varieties of *O. basilicum* and conclude that the variety most suited for cultivation is that of *O. crispum* (curly-leaved basil). The results of the chemical examination are tabulated below. (Crop 1910.)

| Variety | Sp. gr. 15° | Opt. rot. | Ref. ind. 20° | Esters[1] % | Alcohol[2] % |
|---|---|---|---|---|---|
| Thyrsiflorum......... | 0.9168 | −10.85° | 1.488 | 1.96 | 35.19 |
| Crispum.............. | 0.9123 | −10.5° | 1.484 | 1.71 | 35.19 |
| Album............... | 0.8975 | −12.9° | 1.479 | 1.71 | 39.66 |
| Purpurascens....... | 0.8959 | −13.85° | 1.477 | 3.43 | 38.46 |

[1] As linalyl acetate.
[2] As linalol.

The methyl-chavicol content of all the oils was approximately 55% (calculated from an estimation of the methoxyl group).

The normal sweet basil oil (*i. e.*, an oil from France, Germany, Spain or Algeria) has the following characteristics.

Sp. gr. 15°................................. 0.900 to 0.930
Opt. rot.................................... −6° to −22°
Ref. ind................................... 1.4800 to 1.4950
Acid value................................ 1 to 4
Ester value %............................. 1 to 12
Solubility 1 to 2 vols. and more 80% alcohol.

Oils of basil from geographical and botanical sources other than those given above have been examined, but they do not appear in quantities in commercial channels.

The constituents of sweet basil oil thus far identified are methyl-chavicol, *l*-linalol, cineole, *d*-α-pinene, *d*-camphor and eugenol.

The oil is used in perfumery.

## Snake-root Oils (Oils of Asarum Europæum and Asarum Canadense)

These 2 oils are the products of the distillation of the rhizomes and roots of *A. Europæum* and *A. Canadense*, respectively. The chief known characters of the different snake-root oils are contained in the following table:

| Oil | Source | Sp. gr. at 15.5° | Other characters and constituents |
|---|---|---|---|
| European snake-root | Rhizome and root. | 1.015 to 1.070 | Brown, aromatic. On long standing, the oil is said to deposit crystals of asarone. Contains lævopinene; methyl-eugenol or -isoeugenol, and a blue-green high-boiling fraction. |
| Canada snake-root | Rhizome and root. | 0.950 to 0.952 | Yellow or yellowish-brown oil of strong aromatic odour. Optical rotation, $-10.5°$ to $-22°$. Contains $d$- and $l$-pinenes (2 %); $d$-linalol; $d$-borneol; $l$-terpineol; geraniol (total alcohols, 35 %); methyleugenol (37 %); a phenol, $C_2H_{12}O_2$; a lactone, $C_{14}H_{20}O_2$; a mixture of fatty acids, including acetic and palmitic; a blue oil, consisting of oxygenated substances of an alcoholic nature (about 20 %). |
| Virginia snake-root | Whole herb of *Aristolochia serpentaria*. | 0.980 to 0.990 | Contains an ester of borneol. |
| . . . . . . . . . . . . | Root of *A. reticulata*. | 0.974 to 0.978 | Optical rotation $= -4°$; contains pinene and borneol. |
| . . . . . . . . . . . . | Root of *A. clematis.* | About 0.910 | A thick yellow oil. |
| . . . . . . . . . . . . | Dried herb of *Asarum arifolium.* | 1.0585 to 1.0613 | Optical rotation, $-2.5°$ to $-3.7°$. Contains safrol (chief constituent); lævopinene; eugenol; a phenol; methyl-eugenol and methyl-isoeugenol; asarone, and a sequiterpene. |

It would appear that a further investigation of the composition of some of the oils is desirable, although they are not of any great importance. Our present knowledge of them, as given in the above table, is chiefly due to the researches of F. B. Power (*Proc. Amer. Phram. Assoc.*, 1880, **28**, 464); Petersen (*Arch. Pharm.*, 1888, **226**, 123) and Power and Lees (*J. Chem. Soc.*, 1902, **81**, 59).

## Thyme Oil

This oil is obtained by the distillation of *Thymus vulgaris*, and is produced largely in France. Spanish oil is also an article of commerce but the plant from which it is distilled is uncertain. (Consult *Perf. & Ess. Oil Record*, 1920, 338, Spanish oil of thyme, by E. M. Holmes.)

The French oil is the more valuable. In the south of France the oil not infrequently suffers admixture with the oil of *Thymus serpyllum* and with French oil of turpentine.

Two varieties of oil of thyme, namely the "red" and "white," are known in commerce. The name usually applied in pharmacy to oil of thyme, which is frequently used in liniments especially by veterinary practitioners, is oil of origanum. True oil of origanum is of different physical and chemical properties, and is obtained from *Origanum vulgare*, *O. hirtum*, and *O. Smyrnæum*.

In reference to oils of origanum, which are naturally dealt with under thyme oil, it should be noted that the various species of this plant have been described so loosely by different botanists that the mere specific name is valueless without the addition of the name of the authority.  Thus there are three different species bearing the name *Origanum creticum,* and two each described as *O. hirtum,* and *O. smyrnæum.*  The species from which the oil has been actually distilled and examined are as follows:

> *Origanum majoranoides*—Willd.
> *Origanum onites*—Linn.
> *Origanum maru*—Linn.
> *Origanum hirtum*—Link.

The oil from *Origanum majoranoides* Willd contains a large amount of phenols, consisting almost entirely of carvacrol.  The oil has the following characters:

Sp. gr..................................... 0.962 to 0.9685
Rotation.................................... 0° to +1°
Phenols.................................... 70–80%

It is soluble in 2.5 to 3 volumes of 70% alcohol.  The oil from *Origanum onites* has a sp. gr. 0.948, rotation −10° 15′, and phenol value 68% (*Bull. Imp. Inst.,* 1911, **9**, 388).

The characters of the oil of *Origanum hirtum* are doubtful, but according to recent investigations it contains thymol and no carvacrol, although Jahns in 1879 (*Arch. d. Pharm.,* 215, 1) stated that this oil contained carvacrol as its chief constituent.  It is probable that Jahns' oil was misdescribed.  A sample examined by the Imperial Institute (*Bull. Imp. Inst.,* 1911, **9**, 383) had a sp. gr. 0.944, optical rotation +0° 24′, and phenol value 66–67%.  Three distillates from *Origanum hirtum albiflorum, Hassk* had the following characters:

Sp. gr..................................... 0.923–0.940
Rotation.................................... +0° 6′ to 0° 8′
Ref. index................................. 1.4939 to 1.5044
Phenols.................................... 51–60%

The unrectified ("red") oil is stated to owe its colour to the action of the phenolic constituents of the oil on the iron of the apparatus employed in the distillation.  The oil can be rectified to a light yellow-coloured oil ("white oil of thyme").  The sp. gr. of thyme oil ranges from about 0.905 to 0.950.  It is slightly lævorotatory,

to −4° for 100 mm.   Parry gives the ref. index as 1.4800.   It is soluble in half its volume of 90% alcohol, in 1 to 2 volumes of 80%, whilst with from 15 to 30 volumes of 70% alcohol most genuine thyme oils afford a clear solution.

The main constituents, are the phenols thymol and carvacrol; the alcohols linalol and borneol; bornyl acetate; cymene, and lævopinene.

Thymol and carvacrol do not appear to be constantly present together in thyme oil.   The conditions under which one or other of these isomeric phenols is present are not definitely known.   Schimmel & Co. found that the oil from dried French thyme contained much thymol, but only a little carvacrol.   French and dried thyme (German) gave oils containing only thymol.

Spanish thyme oil contains from 30 to 60% of phenols, mostly carvacrol.   It is often mixed with French oil to increase the lower phenol content of the latter.

The *phenolic constituents* of thyme oil are perhaps the most important, although there is no doubt that the borneol and linalol contribute to the odour of the oil.   The percentage of thymol and carvacrol in thyme oil is usually about 20 to 30, and should never fall below 20%.   The phenols may be estimated approximately by noting the proportion dissolved by sodium hydroxide solution, or by observing the amount of distillate obtained above 220°.   This should not be less than 25% of the oil.
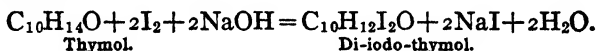
The U. S. P. (9th Rev.) requires thyme oil to contain at least 20% by volume of phenols, the oil being assayed by shaking 10 c.c. of the sample in a cassia flask with 25 c.c. of 5% sodium hydroxide solution, and setting the mixture aside for 12 to 24 hours.   The volume of unabsorbed (non-phenol) oil is then noted, and the proportion of phenols deduced.

The following method for the estimation of the phenols in thyme oil is due to Kremers and Schreiner (*Pharm. Rev.*, 1896, 14, 221).   The method is in reality a modification of that of Messinger and Vortmann (*Ber.*, 1890, 23, 2753).

5 c.c. of the oil to be examined are weighed and introduced into a burette.   The oil is diluted with about an equal vol. of petroleum spirit, when a 5% solution of potassium hydroxide is added and the mixture vigorously shaken for a short time.   The liquid is then allowed to stand until separation is complete.   The alkaline solution

is now run off into a 100 c.c. flask. The agitation with the alkali is repeated until no further diminution of the volume of the oil occurs.

The alkaline liquid containing the dissolved thymol is now made up to a definite volume (100 or 200 c.c.) with 5% potassium hydroxide solution. An aliquot portion of this liquid (say 10 c.c.) is next introduced into a 500 c.c. flask, and N/10 iodine solution added in slight excess. In order to determine whether an excess of iodine has been added, a few drops of the liquid in a test-tube should be treated with a little dilute hydrochloric acid. If insufficient iodine has been added, the liquid will become milky owing to the separation of thymol. In the presence of an excess of iodine, a brown colour only will be seen. The thymol combines with the iodine, and a reddish-brown precipitate is produced. When excess of iodine has been added, the liquid is rendered slightly acid with dilute hydrochloric acid, and diluted to 500 c.c. with water. $\frac{1}{5}$ of the liquid (100 c.c.) is now filtered off, and titrated with N/10 sodium thiosulphate solution. Each c.c. of N/10 iodine solution is equivalent to 0.003741 grm. of thymol, the reaction which occurs being represented by the following equation:

$$C_{10}H_{14}O + 2I_2 + 2NaOH = C_{10}H_{12}I_2O + 2NaI + 2H_2O.$$
$$\underset{\text{Thymol.}}{\hspace{2.5cm}} \underset{\text{Di-iodo-thymol.}}{\hspace{3.5cm}}$$

In the case of carvacrol, a finely divided white precipitate is produced with the iodine solution. The liquid is therefore vigorously shaken after the addition of the iodine solution and then filtered. The filtrate is next acidified with hydrochloric acid, and the process continued exactly as in the estimation of thymol. Since thymol and carvacrol are isomeric methyl-propyl phenols, and the same reaction occurs in both cases, the calculation in the case of the latter is the same as for thymol.

"White" French thyme oil is said to be almost invariably of poor quality and, as has been stated, is frequently adulterated with French oil of turpentine. Such adulterated oils would be strongly lævorotatory. The addition of the oil from *Thymus serpyllum* (wild thyme) to genuine thyme oil also increases the rotation (see table on page 140).

The abstraction of thymol from thyme oil is much practised, and it is therefore important to estimate, at least approximately, the proportion of phenols present in the oil, as described on page 509. On the other hand, the phenols are not the only constituents

contributing to the odour of thyme oil, since linalol and borneol are present to the extent of about 5 and 8%, respectively. Thyme oils which have suffered abstraction of the greater part of their thymol frequently possess a very fair odour. The addition of *phenol* to thyme oil according to the U. S. P., (9th Rev.) may be detected by agitating the oil with a little *hot* water, when no blue or violet colour should be produced in the aqueous liquid on the addition of ferric chloride solution.

The less important varieties of thyme oil are described in the following table:

| Oil | Botanical source. Root of: | Sp. gr. | Opt. rot. | Characters and constituents |
|---|---|---|---|---|
| Wild thyme...... | *Thymus serpyllum* | 0.890 to 0.920 | $-10°$ to $-21°$ | Cymene; a sequiterpene; one or more phenols. |
| ............... | T. capitatus | | | |
| ............... | T. camphoratus | About 0.900 | ........ ..... | Pinene; cymene; dipentene; thymol (?); carvacrol (?); bornyl acetate. |

### Turpentine Oil (Spirit of Turpentine)[1]

Oil of turpentine is contained in the wood, leaves and other parts of pines, firs and other coniferous trees.

Commercial turpentine oil, known also as "turpentine," "spirits of turpentine," "gum spirits" and, by the painter, simply as "turps," is produced chiefly by the aqueous distillation (distillation with water by direct heat, or by steam distillation) of the crude turpentine (oleo-resin) derived from various species of *Pinus*.

The oleo-resin is produced by a physiological process in the sapwood of the tree, as the result of incisions made periodically during the summer season. The non-voltatile portion constitutes *rosin* or *colophony* (page 242). The distilled oil, varying in yield from 10 to 25%, after separation from the aqueous distillate, is an almost colourless or often slightly yellowish liquid, very mobile, with a characteristic odour and a pungent, biting taste. The oil thus produced is the only kind recognised in the various pharmacopœias and dispensatories as suitable for medicinal uses.

For certain purposes *rectified oil of turpentine* is requisite. This is produced by treating the ordinary product with alkali, to saturate any acids, and redistilling, preferably in a current of steam.

[1] Revised by F. P. Veitch and V. E. Grotlisch.

Vèzes, under the authority of the Executive Committee of the White Cross Congress held in Paris in 1909, has suggested the following standards for commercial oil of turpentine.

Turpentine oil is the exclusive product of the aqueous distillation (distillation with water or non-superheated steam) of the turpentine derived from various species of *Pinus*. It is a colourless, often slightly yellowish or greenish, liquid, very mobile, with a characteristic odour. Under a normal pressure of 760 mm., the oil begins to boil between 152 and 156°; at least 80% by weight must have passed over at 164°. The oil should be neutral or give only a faint acid reaction; the permissible acid-content, estimated with phenolphthaleïn as an indicator, must not exceed 1.5 grm. pure potassium hydroxide (KOH) for every kilogram of oil. The oil must also be free from mineral oils and, in fact, from all substances other than those generated in the course of the aqueous distillation of turpentine. It may contain small proportions of resin-oil and colophony, resulting from the process of manufacture, but the aggregate weight of these may not exceed 2.5%.

In addition to the ordinary oil of turpentine, two other kinds are produced which are used for industrial purposes. Steam-distilled wood turpentine oil is obtained in the United States by extraction of pine saw dust or finely ground resinous waste wood (called lightwood), with superheated steam.

Destructively distilled wood turpentine oil (sometimes called stump turpentine) is obtained from the same sources by a process of destructive distillation with direct heat at high temperatures. By far the largest proportion of the world's supply of turpentine oil is made from the exuded oleo-resin.

From 60 to 65% of the world's supply of oil of turpentine is produced in the United States, of which about 90% is obtained from crude turpentine. Most of the balance of the world production comes from the following countries, given in the order of their importance under normal conditions: France, Russia, Spain, Greece, Portugal, Sweden, Finland, India. The French, Spanish, Grecian, Portugese and Indian oils are made from the crude turpentine gum, or oleo-resin, while those from Russia, Sweden and Finland are chiefly destructively distilled oils.

In addition, turpentine oil is also produced on small commercial scales in Mexico, Austria, Italy, Norway, China, Germany, Poland,

French Indo-China, Central America, Japan, Algeria and British South Africa; that of Norway and Poland being chiefly destructively distilled from stump wood.

**American turpentine oil** is produced in the southern part of the United States from the oleo-resin of the southern longleaf yellow pine (*Pinus palustris*), and the Cuban or slash pine (*Pinus caribœa or heterophylla*).

Here and there the rosemary pine (*P. tœda*) is tapped where it occurs singly or in small groups among the other kinds. Both kinds of wood turpentine oils are obtained from the partly decayed stumps and logging waste of the same varieties.

The main constituent of American turpentine is $d$-$\alpha$-pinene, the balance being mostly $d$-$\beta$-pinene or nopinene, with small quantities of higher terpenes and complex sesquiterpenes.

**French turpentine oil** is made from the crude turpentine yielded by the maritime or cluster pine (*Pinus maritima* or *pinaster*) growing in the lowlands of the Gironde and Landes regions. In contrast with the method of distillation used in the United States, where direct heat distillation is employed almost exclusively, most of the large French turpentine distilling plants operate on the steam distillation process. According to G. Dupont (*Chem. et Ind.*, 1922, **8**, 549) French turpentine oil, after neutralisation and rectification, consists of approximately 63% of $l$-$\alpha$-pinene, 26.5% of $l$-$\beta$-pinene or nopinene, and 10.5% of residue containing dipentene, sobrerol, pinol, a ketone and a high boiling, unidentified, strongly dextrorotatory sesquiterpene.

**Russian oil of turpentine** is chiefly the product of *Pinus sylvestris*, the Scotch fir, but *P. Ledebourii* and other species also contribute to it. This oil is made mostly by destructive distillation on a small scale by the peasants, and is usually poorly rectified and very variable in character, the normal constituents being accompanied by more or less of the products of destructive distillation both of the rosin and of the wood, including benzenoid hydrocarbons, phenoloid substances, furfurane and sylvane.

A sample of Russian turpentine oil was found to contain 10 to 15% of pinene, 65 to 70% of sylvestrene, a considerable quantity of cymene and small proportions of high-boiling viscous hydrocarbons. The odour is strong and penetrating, entirely distinct from that of American and French turpentine oil. It is not generally

used in paint, though there does not appear to be any good reason against the use of the refined Russian oil for this purpose. The oil finds a special application, under the name of "tar spirits," as a solvent for cottonseed oil pitch for the manufacture of tar varnishes.

The results of Parry's investigations in regard to Russian turpentine confirm the fact, which is stated by Professor Schindelmeister of Dorpat University, that most of the Russian turpentine oil of commerce has had the early runnings removed for home consumption, later fractions being then exported.

The following figures are those of a number of Russian turpentines on the London market.

|  | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| Initial b. p. | 157° | 156° | 157° | 158 |
| Distils below 155° | none | none | none | none |
| Distils 155°–160° | 1% | 1% | 5% | 11% |
| Distils 160°–165° | 44% | 45% | 40% | 18% |
| Distils 165°–170° | 37% | 35% | 42% | 48% |
| Distils 170°–180° | 15% | 16% | 10% | 19% |
| Distils above 180° | 3% | 3% | 3% | 4% |
| Sp. gr. at 15° | 0.863 | 0.8635 | 0.863 | 0.868 |
| Ref. ind. at 20° | 1.4730 | 1.4726 | 1.4725 | 1.4748 |
| Opt. rot. | +4° 28' | +4° 30' | +9° | +8° |
| Absorbed by 5% KOH | nil | nil | nil | nil |

A very large number of samples, however, have been more largely deprived of their early runnings, and contain a considerable amount of hydrocarbons boiling above 180°, and also a considerable amount of acid substances, which are absorbed by potassium hydroxide. Such samples are quite useless to the rectifier, as their redistillation must ensure the removal of the acid substances and also of the substances boiling above 180°, with a resulting loss which causes the rectification to be unremunerative.

Parry gives the following figures for two samples of virgin crude Russian turpentine:

|  | I | II |
|---|---|---|
| Sp. gr. | 0.867 | 0.865 |
| Optical rotation | +7° 50' | +10° |
| Ref. index | 1.4718 | 1.4736 |
| Absorbed by 5% KOH | 5% | 6% |
| Distilled below 155° | traces only | traces only |
| Distilled 155°–160° | 65% | 63% |
| Distilled 160°–165° | 11% | 9% |
| Distilled 165°–170° | 13% | 15% |
| Distilled 170°–180° | 7.5% | 7% |
| Distilled above 180° | 3.5% | 6% |

From these two samples the tarry and acid substances were removed and the rectified sample, in the case of No. I had the following characters:

Sp. gr............................................. 0.8646
Optical rotation.................................... +8°
Ref. ind........................................... 1.4890
Absorbed by KOH.................................. none
Distils below 155°................................. none
Distils 155°–160°.................................. 68%
Distils 160°–165°.................................. 13%
Distils 165°–170°.................................. 10%
Distils 170°–180°.................................. 7%
Distils above 180°................................. 2%

A small quantity of turpentine oil is produced in the Archangel and Vologda governments by distillation of a hardened oleo-resin known as *sierra turpentine*, collected from *Pinus sylvestris*. It is produced by wounding the tree somewhat in the French style, and is collected twice a year.

Both the yield and quality of the oil distilled therefrom is low, as compared with the American and French oils.

**Swedish, Finnish and Norwegian turpentine oils** are obtained from the same source as Russian oil of turpentine and are quite similar to it. Some turpentine oil is also produced in Sweden as a by-product in the manufacture of paper pulp by the sulphite process, but the quantity is not large.

**Finland Turpentine Oil.**—The following results of the examination of 3 samples of turpentine oil from Finland have been published by Aschan and Hjelt (*Chem. Zeit.*, 1894, **18**, 1566). The oil is obtained from the trunks and roots of *Pinus sylvestris* and *P. abies*, the distillation being conducted at a high temperature. The crude oil is freed from acetic acid and tarry matters by distillation over lime.

**Oil from South Finland.**—Fractional distillation yielded 7.1% boiling at from 155° to 160°; 30.2% boiling at from 160° to 165°; 22.6%, b. p. from 165° to 170°; and 20.1% boiling from 170° to 175. The first fraction consists chiefly of pinene, the higher fractions chiefly of sylvestrene and dipentene. This turpentine oil is therefore identical in composition with Swedish and Russian oils.

**Oil from North Finland.**—The bulk of this oil distils between 170° and 178°. The lower-boiling portions consist chiefly of pinene, but the larger proportion of the oil consists of dipentene with scarcely any sylvestrene.

**Spanish and Portuguese turpentine oils** are obtained from the oleoresin of the Calabrian pine, a variety almost identical with the French *Pinus pinaster*, but showing some variations due to difference in climate and soil. The chemical composition and properties are practically the same as those of the French oil.

**Indian turpentine oil** is obtained from the chir pine, *P. longifolia*, and the Himalayan or Bhotan pine, *P. excelsa*, the former being the more important. It is somewhat heavier than American oil of turpentine. An authentic oil examined by Simonsen (*J. Chem. Soc.*, 1920, **117**, 570) had a sp. gr. at 30° of 0.8717; ref. ind. at 30°, 1.4725, and a spec. rot. of −2.38°. Besides $\alpha$- and $\beta$-pinene, it contained *d*-carene and a sesquiterpene, longifolene. To the presence of these two higher terpenes is ascribed the ease of oxidation and high evaporation residue shown by Indian turpentine oils. Improvements in rectification have enabled the Indian turpentine distilleries to separate the oil into two or more fractions, so that some Indian turpentine oils are now found to be of good quality. There is little or no exportation of the oil from India.

**Grecian oil of turpentine** is distilled from the oleoresin of the Aleppo pine, *P. halepensis*. This tree is common throughout Greece, and it also serves as a source of turpentine oil in Algeria and parts of Asia Minor. In Greece large quantities of the oleroresin are used to flavour the native wines, to which it imparts a peculiar terpene flavour. After serving this purpose, the gum is recovered and distilled. Certain esters are in turn absorbed from the wine, which give Grecian turpentine oils an agreeable, vinous odour. According to G. Dupont (*Compt. rend.*, **174**, 395) turpentine oil from *P. halepensis* consists of about 95% of dextro-$\alpha$-pinene, 3.8% of sesquiterpenes, and 1.1% of bornyl esters. Two authentic samples examined by Parry (*Perf. and Ess. Oil Rec.*, 1912, **2**, 210) had densities of 0.8605 and 0.8620, spec. rot. of +36.75° and +39°; and ref. ind. of 1.4690 and 1.4736 at 20°. Both distilled at 156°.

Small quantities of turpentine oil are obtained from a variety of this tree in Southeastern France.

**German turpentine oil** is produced by distillation of the oleoresin of *Pinus sylvestris*. This industry had its beginning in 1916, when the supplies of turpentine and rosin from without the boundaries of Germany were largely cut off by the Allied blockade. The German oil is of good quality, but the yield per tree is not great enough for

the industry to compete with imported oils from France and America without the aid of a state subsidy.   Henrich (*Zeit. angew. Chem.*, 1921, **34**, 363) obtained from authentic samples of the fresh oleoresin yields of 21.8% to 24.7% of volatile oil, having densities at 20° of 0.8464 to 0.8573; spec. rot. of +11.32° to 16.10°; the oils boiled at 150°–155°, and consisted of α-pinene and β-pinene, together with small proportions of dipentene, sylvestrene, esters and traces of a free acid.   Both dextro- and lævo-pinene were present, the former predominating.

**Mexican turpentine oil** is obtained from the oleoresin of the Ocote pine, *P. teocotl*; the Western yellow pine, *P. ponderosa*; and the Mexican white pine, *P. ayacahuite*.   It contains about 90% of pinene, and has a very aromatic pleasant odor.   The sp. gr. of four samples examined in the U. S. Bureau of Chemistry was found to be 0.8634 to 0.8669 at 15.5°, with ref. ind. at 20° of 1.4658 to 1.4686.   The rate of evaporation and the residue are similar to those of American oils.

### Turpentine Obtained by Distilling Resinous Wood with Steam

Considerable quantities of oil of turpentine are produced in the United States by distilling resinous wood with super-heated steam. The crude oil thus obtained is much easier to rectify and gives a more pleasant-smelling product than the destructively distilled oil of turpentine.

The chief fraction distils between 155° and 160° and contains much pinene.   In the higher fractions sylvestrene is found, but rarely dipentene.   The latter is found, however, in the crude oil produced by destructive distillation, or when superheated steam at high pressure is used.   From this it is concluded that dipentene is not a natural product, but is formed by the superheating of the pinene during the process of distillation.

Steam-distilled wood turpentine oils usually contain small quantities of mineral oil, due to the process of manufacture, in which the rosin and less volatile portions of the pine oil are extracted from the wood, after distillation of the turpentine oil with steam, by means of hot gasoline.   Portions of this solvent are held by the apparatus, and get into the next charge of turpentine oil.   The lighter fractions recovered from the extracted pine oil also contain traces of the mineral solvent.   For this reason a slightly larger polymerisation residue is permitted with this class of turpentine oil.

### Characteristic Properties and Examination of Turpentine Oils

While exhibiting certain characteristic differences in certain respects (*e. g.*, optical activity, b. p.), oils of turpentine from different sources present a rather close general similarity.

The odour of turpentine oil is peculiar and characteristic, and in some instances rather aromatic, as in the case of Mexican oil of turpentine. The odour of both steam-distilled and destructively distilled wood turpentine oils are distinct and different from that of gum spirits. Steam-distilled oil has the peculiar odour of fresh pine sawdust, and is probably due to certain substances, extracted from the wood, which are closely related to pine oil. Destructively distilled oil has an odour of the decomposition products of the wood and the resin contained therein.

According to H. Schiff (*Chem. Zeit.*, 1896, **20,** 361), the odour commonly associated with oil of turpentine is due to the presence of a small proportion (under 1%) of an aldehydic oxidation product, which is formed when the oil is exposed to a feeble light in an imperfectly closed vessel. On treating the oil with sodium hydrogen sulphite solution this substance is removed, and the purified oil retains only a slight ethereal aroma; but the characteristic odour soon returns if the oil is exposed to the air. It is a noteworthy fact that the odours of American, French, and Russian turpentine oils are quite distinct.

Oil of turpentine is readily combustible, burns with a very smoky flame, is almost wholly insoluble in water, glycerol, and dilute alkaline and acid solutions. It is very soluble in absolute alcohol, but the solubility is greatly reduced by the presence of water, spirit of 0.850 sp. gr. dissolving only 10% of its weight.

It is very soluble in (probably miscible in all proportions with) ether, carbon disulphide, chloroform, benzene, petroleum spirit, and fixed and essential oils.

Turpentine oil, even when clear, is never wholly free from water, and on distillation the first fractions are usually turbid. The ready formation of hydrogen peroxide in presence of turpentine oil and its subsequent decomposition into oxygen and water, may account for this fact.

Turpentine oil absorbs oxygen on exposure to air, gradually becoming viscid and ultimately resinous. It is this property which gives turpentine oil its peculiar value—not shared by its substitutes

—to the painter and varnish-maker, since it acts as an oxygen-carrier to the drying oil, and the resin formed acts as a binding material for the pigments with which it is mixed.

Turpentine oil in contact with water is gradually converted into *terpin hydrate*. When acted on by sulphuric acid terebene is produced (page 181).

Chlorine and bromine combine with oil of turpentine with such energy that inflammation frequently occurs, with separation of carbon. When dissolved in carbon tetrachloride or chloroform, turpentine oil absorbs very nearly 2 molecules of bromine. Iodine is dissolved by turpentine oil to form a brown solution, which ultimately becomes hot and gives off hydriodic acid; and when considerable quantities of iodine and turpentine oil are suddenly brought together, explosion frequently ensues. When distilled with bleaching powder and water, turpentine oil yields a considerable proportion of chloroform.

Moderately strong nitric acid oxidises turpentine oil to resinous substances, which ultimately yield terebic acid, terpenylic acid, oxalic acid, acetic acid, and other products. Ordinary turpentine oil yields terephthalic and paratoluic acids in addition, but these products are chiefly due to the oxidation of the cymene present, and are formed in traces only by the oxidation of pure pinene. Fuming nitric acid acts very violently on oil of turpentine, often setting it on fire.

Strong chromic acid mixture oxidises turpentine oil, chiefly to acetic acid, but a weaker reagent produces terpenylic acid. If cymene be present, terephthalic acid appears among the products of the oxidation.

Turpentine oil unites readily with hydrogen chloride gas, with evolution of heat, to form pinene hydrochloride. If the gas is dried and the turpentine kept cold, the yield of the hydrochloride is high, and the oil changes on standing in the cold to an almost solid mass. Pinene hydrochloride is a crystalline white substance readily volatile on standing exposed to the air, and having an odour much like that of camphor. This is the first step in the manufacture of synthetic camphor from oil of turpentine.

The sp. gr. of turpentine oil varies from about 0.860 to 0.875, depending on its source and composition, and also on its age and the conditions under which it was stored. The absorption of oxygen

and increase in sp. gr. take place more readily when the oil is exposed to light. Pure alpha-pinene, the principal constituent of most oils, has a sp. gr. of 0.858 to 0.860 at 20°. Beta-pinene, another important constituent has a sp. gr. of 0.867. The following table shows the sp. gr. of most of the various kinds of industrial oils produced throughout the world, including the widest range observed in genuine commercial samples.

| Kind of oil | Sp. gr. at 15.5° | No. of samples | Observer | Reference |
|---|---|---|---|---|
| American.......... | 0.8650 to 0.8695 | 20 | A. Wilson | *Chem. Tr. J.*, 1888, **6**, 316 |
| American (commercial samples) | 0.8656 to 0.8748 | ........ | J. H. Long | *Chem. Tr. J.*, 1892, **10**, 261 |
| American (authentic fresh oils). | 0.8659 to 0.8722 | 67 | A. W. Schorger | *J. Ind. Eng. Chem.*, 1914, **6**, 543 |
| American.......... | 0.8620 to 0.8750 | ........ | U. S. Federal Spec. Board | *Bur. Stand. Circ.* 86 |
| French............ | Not less than 0.8575 at 25° | ........ | Vezes | ......................... |
| Spanisn........... | 0.862 | 1 | O. Fernandez | *Chem. Ztg.*, 1911, **35**, 1152 |
| Grecian........... | 0.8605 to 0.8672 | 5 | Dambergis E. J. Parry Utz, et. al. | *Österr. Chem. Ztg.*, 1904, 14 *Apoth. Ztg.*, 1904, **19**, 678 *Perf. & Ess. Oil Rec.*, 1901, **2**, 210 |
| German........... | 0.8630 | 1 | R. Henrich | *Chem. Ztg.*, 1916, **40**, 673 |
| Norwegian........ | 0.866 | 1 | O. M. Halse & S. Samuelson | *Tidskrift Kemi*, 1918, **15**, 177 |
| Italian (from *P. pinea*). | 0.8473 to 0.8580 | ........ | F. C. Palazzo | *Ann. Chim. Applic*, 1916, **6**, 135 |
| Indian............ | 0.866 to 0.871 | 3 | F. Rabak, et. al. | *Pharm. Rev.*, 1905, **23**, 229 *Bull. Imp. Inst.*, 1911, **9**, 8 |
| Russian........... | 0.8620 to 0.8722 | ........ | C. T. Kingzett | *J. Soc. Chem. Ind.*, 1886, **5**, 10 |
| Russian (from oleo-resin). | 0.8670 | 1 | Schkatelow | *Monit. Scient.*, 1908, IV, **22** 217 |
| Finnish........... | 0.861 | 1 | Utz | *Chem. Rev. Fett-Harz. Ind.*, 1905, **12**, 71 |
| Mexican.......... | 0.8634 to 0.8669 | 4 | U. S. Bur. Chem. | Communicated |
| Japanese (from *P. Thunbergii*). | 0.8740 | 1 | Y. Shinosaki | *J. Chem. Ind. Tokio*, 1918, **21** 763 |

Italian oil obtained from *Pinus pinea* has a much lower sp. gr. than other turpentine oils. This is due to the presence of a large proportion of limonene, which has a sp. gr. of 0.844 to 0.846 at 20°. The distillation temperature and opt. act. are considerably higher than those for most turpentine oils, for the same reason.

The higher values shown for Japanese oil of turpentine from *P. Thunbergii* are due to large proportions of camphene and high boiling sesquiterpenes.

The sp. gr. may in itself be sufficient to indicate the presence of any considerable proportion of some adulterants of turpentine oil, but it is not of much value for quantitative purposes, owing to the variable character of shale and petroleum products. In fact, heavier fractions of shale oil and petroleum are apt to be added to turpentine oil, although their presence is still more objectionable than the naphthas.

Oil of turpentine is optically active, both positively and negatively, depending on the source. The opt. act. of pure oils varies within such wide limits, and is affected by so many factors, that a determination of this property is of little value in the analysis of oil of turpentine except for throwing light on the origin of a sample. The optical activities of turpentine oils from various sources are shown in the following table:

| Kind of oil | Spec. opt. rotation | Authority |
|---|---|---|
| Pure *d*-pinene (alpha)..................... | $+21.5°$ | W. A. Tilden |
| Authentic American from Pinus palustris... | $-1.0°$ to $+19.5°$ | Chas. H. Herty |
| Authentic American from Pinus hetero-phylla.................................. | $+0.25°$ to $-29.4°$ | Chas. H. Herty |
| Commercial American..................... | $-2.0°$ to $+29.6°$ | J. H. Long |
| Pure *l*-pinene (alpha).................... | $-40.4°$ | W. A. Tilden |
| Pure *l*-pinene (alpha).................... | $-43.5°$ | A. Pariselle |
| Pure *l*-pinene (beta)..................... | $-19.8°$ | A. Pariselle |
| Commercial French oil.................... | $-29°$ to $-33°$ | H. E. Armstrong, et al. |
| Spanish (P. pinaster) [1]................... | $-8.73°$ | O. Fernandez |
| Grecian (P. halepensis)................... | $+36.75°$ to $+41°$ | E. J. Parry, Schimmel & Co., et. al. |
| German (P. sylvestris)................... | $+11.32°$ to $+20.99°$ | R. Henrich |
| Polish (P. sylvestris)..................... | $+15.4°$ to $+24°$ | Flawitzky |
| Russian (P. sylvestris)................... | $+15.0°$ to $+23.4°$ | H. E. Armstrong |
| Indian (P. longifolia).................... | $-0.7°$ to $-2.38°$ | J. I. Simonsen, et. al. |
| Italian (P. pinea)....................... | $-72.5°$ to $-97.3°$ | F. C. Palazzo |
| Mexican (P. ayacahuite)................. | $+21°$ to $+40.4°$ | U. S. Bur. Chemistry |
| Japanese (P. Thunbergii)................. | $-19.3°$ | Y. Shinosaki |

[1] According to the author, Oil from *P. halepensis* was apparently present.

It will be noted that the observed optical rotations of commercial oils of turpentine differ considerably from the sp. rotatory powers of the terpenes said to form their chief constituents. J. H. Long (*J. Amer. Chem. Soc.*, 1899, **21**, 637) has pointed out that the optical activity of commercial oil of turpentine of American origin is far more irregular than is commonly assumed. Thus, while the great majority of specimens of American oil exhibit a marked dextrorota-

tion, samples are occasionally met with which are only feebly dextrorotatory or which even exhibit lævorotation. In 2 cases the dextrorotation reached 29.6° and 25.1°, respectively, an activity which is greater than that attributed by Tilden to pure australene. Out of forty samples examined by Long (some of which were American oils of commerce and others prepared by him in the laboratory by distilling the fresh oleo-resins in copper with water) 3 samples exhibited lævorotation (−2.02°, −34.83°, and −16.92°). Long finds the oil from the so-called *spruce pine*, by which he probably meant the Cuban or slash pine (*P. heterophylla*) to be strongly lævorotatory, the angular rotation in a 200 mm. tube ranging from about −63° to over −70°. On fractionally distilling the oil, the portions first passing over showed an angular rotation of −69° to −73° (for 200 mm.), which fell in the fractions of higher b.p. to about 10° less. Long has further shown that the rotation of the fractions of oil of turpentine frequently becomes less and less in the higher fractions. In one case the optical rotation fell to 2°, while another sample gave on distillation, a first fraction which had a rotation of −16.8° and a twelfth fraction having a rotation of −4.4°. The observation of Marsh and Gardner (*J. Chem. Soc.*, 1891, **59**, 725) that the first fractions obtained by the distillation of turpentine oil have a greater optical activity than those of higher b. p., are thus confirmed.

Long suggested that the lævorotation sometimes exhibited by American turpentine oil may be due to products from slash pines, especially from trees in the district around Mobile. He points out that in numerous oils known to be free from slash a marked dextrorotation was always observed, while low dextrorotation was limited to oils distilled in districts where the slash-pine is occasionally found. Long affirms that turpentine from the same tree contains lævo- and dextropinene in varying proportions.

The observations of Dr. Chas. H. Herty (*J. Amer. Chem. Soc.*, 1908, **30**, 863) amply prove this statement. The oil from a certain tree which was feebly rotatory, at one season gave a dextro-rotation, and later during the same season a lævorotation. He found that with one exception, the oils from slash pines were lævo-rotatory, and those from *P. palustris* dextro-rotatory.

The *index* of *refraction* of turpentine oil is a useful indication of its purity, especially in confirmation of other tests. Genuine oil

of turpentine was found by T. Macfarlane (*Canadian Inland Rev. Dept.*, 1901, *Bull.* 79) to have a ref. index ranging from 1.4667 to 1.4722 at 20°. Oil which has been exposed to light and air for some time may have a higher ref. ind. up to 1.478. Rosin spirit ("spiritine") has a similar refractive index, while light petroleum products and kerosene have lower refractive indices than oil of turpentine (see table, page 155). Macfarlane's observations were made at the temperature of the laboratory, and were corrected to 20° by the addition or subtraction of 0.0005 for each 1° above or below this temperature. The instrument was an Abbé-Zeiss refractometer, and was adjusted to read 1.3330 for water at 20°.

J. H. Long (*Chem. Trade Jour.*, 1892, **10**, 261) suggested the determination of the vapour density of turpentine oil as a method for its technical examination. A specimen of the pure oil was distilled, and about 0.150 grm. of the fraction passing over between 155.5° and 156.5° examined by the V. and C. Meyer method (*Ber.*, 1878, **11**, 2253), ethyl benzoate being used as the heating liquid. Two experiments showed a vapour density of 4.68 and 4.66, corresponding to molecular weights of 135.1 and 134.5. Unfractionated commercial turpentine oil showed vapour densities ranging from 4.73 to 5.11. Samples of light petroleum products naturally gave lower figures.

B. Redwood has stated that the presence of petroleum spirit in turpentine oil is readily and certainly indicated by the reduced flashpoint of the sample. Thus, while genuine American turpentine oil flashes at 33.3°, the addition of as little as 1% of ordinary petroleum spirit lowers the flash-point by about 12.2°. This statement has been traversed by Parry, who finds that the flash-point of genuine turpentine oil, as determined by Abel's close-test apparatus, ranges from 33.3° to 37°. Archbutt states that genuine oil of turpentine flashes at 32.2°.

When determined with the Tagliabue closed cup apparatus, which has been adopted as standard for volatile mineral oils by the American Society for Testing Materials, the flash-point of pure turpentine oil is about 33° to 35°.

J. H. Long, in a valuable paper (*Chem. Tr. J.*, 1892, **10**, 261), has given the flash-points and densities of mixtures of 95% of American turpentine oil, flashing at 32°, with 5% of such petroleum products as could be used for the sophistication of turpentine oil.

The flash-point of a mixture is naturally reduced by the presence of the more volatile products, but is actually raised by the oils of higher density.

*Fractional distillation*, if carefully conducted, probably affords more information as to the origin and purity of oil of turpentine than any other physical test, and if the optical activity of the fractions be also observed, further light will be thrown on the nature of the sample. Genuine American oil of turpentine commences to boil at 156°, or within a degree or so of that temperature, the greater part passing over before the thermometer rises above 162°. As a rule, 90% or more passes over before the thermometer rises above 170°, and the distillation should be practically complete below 185°. Russian turpentine oil distils chiefly between 165° and 190.° On the other hand, petroleum, shale, and resin products commence to distil at very varying temperatures, according to their quality, but during the distillation the thermometer rises regularly through a considerable range.

| Product | Sp. gr. | Distillation temperature | |
|---|---|---|---|
| | | Initial | Final |
| Gasolene, 88° B.................... | 0.6508 | About 40° | About 110° |
| Gasolene, 74° B.................... | 0.7001 | About 55° | About 125° |
| Benzine, 63° B.................... | 0.7306 | About 95° | About 165° |
| "Standard White," 110° fire test..... | 0.7999 | About 130° | Above 360° |
| "Water White," 150° fire test.... .. | 0.7918 | About 140° | About 310° |
| "Headlight," 175° fire test.......... | 0.7952 | About 160° | About 315° |
| Mineral seal oil.................... | 0.8293 | About 230° | Above 360° |
| Paraffin oil...................... | 0.8906 | About 300° | Above 360° |
| Oil of turpentine.................. | 0.8680 | About 156° | About 185° |

The exact behaviour of a sample of turpentine oil on distillation depends materially on the precise manner in which the operation is conducted, and in any series of experiments, the results of which are meant to be comparable, the same conditions should be rigidly observed. Of course, the most perfect separation of the constituents is obtained by the use of a dephlegmator; but, for ordinary purposes, the distillation of the turpentine oil in a retort heated over a naked flame, with the thermometer bulb immersed in the liquid, will be found very satisfactory. The distillation should be conducted exactly in the manner described for the assay of commercial benzols.

## CHARACTERS OF ADULTERANTS AND SUBSTITUTES OF TURPENTINE OIL

| Value | Rosin spirit | | Rectified | Camphor oil | Eucalyptus oil | So-called "Canadian turpentine" | | "Terebo" | "Imported spirit" | "Blended turpentine" | "English distilled turpentine" |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | A | B. Old sample | | | | A | B | | | | |
| Sp. gr. at 15.5° | 0.8569 | 0.8884 | 0.8838 | 0.9135 | 0.8902 | 0.8185 | 0.7844 | 0.8263 | 0.8057 | 0.798. | 0.8188 |
| Distillation temperature: | | | | | | | | | | | |
| 1 c.c. | 148.9 | 142.2 | 160.6 | 180.0 | 129. | 172.2 | 117 | 152.2 | 154.0 | 151.5 | 155.6 |
| 5 c.c. | 155.0 | 150.0 | 167.8 | 188.3 | 162 | 173.9 | 119 | 156.7 | 156.0 | 153.0 | 156.7 |
| 90 c.c. | 197.2 | 249.0 | 279.4 | 226.1 | 189 | 272.2 | 160 | 263.3 | 224.4 | 189.5 | 196.7 |
| 95 c.c. | 210.0 | | 310.0 | 234.4 | 201 | 300 | 162 | 315.6 | 235.6 | 202.0 | 205.6 |
| Iodine value | 272.6 | 178.5 | 166.9 | 136.2 | 116.0 | 172.8 | 162.8 | 58.2 | 2.6 | 31.8 | 107.4 |
| Oil surviving polymerisation test, % | 4.4 | | | | | 46 | 54.9 | | | | |
| Sp. gr. | | | | | | 0.766 | 0.725 | | | | |
| Flash-point (Abel test), °F. | | | 86 | 83 | 86 | 90 | 37 | 72 | 78 | 79 | 81 |

| Value | "English turpentine" | "Siberian turpentine" | "South American turpentine" | Turpentine substitute | Turpentine substitute | "Beadless solvent" | "Beadless solvent" | Petroleum distillate | "Turpolene" | "Patent turpentine," 6 samples |
|---|---|---|---|---|---|---|---|---|---|---|
| Sp. gr. at 15.5° | 0.8570 | 0.8663 | 0.8164 | 0.8162 | 0.8238 | 0.8072 | 0.8093 | 0.7992 | 0.8189 | 0.8005 to 0.8220 |
| Distillation temperature: | | | | | | | | | | |
| 1 c.c. | 151.0 | 162.8 | 154.5 | 164.4 | 162.8 | 156.7 | 162.8 | 157.8 | 160.0 | 154.4 to 163.3 |
| 5 c.c. | 153.9 | 164.4 | 155.0 | 167.2 | 165.0 | 159.4 | 163.9 | 158.9 | 163.3 | 160.0 to 170.6 |
| 90 c.c. | 181.1 | 176.7 | 188.3 | 222.8 | 218.9 | 226.7 | 225.6 | 192.8 | 222.2 | 232.0 to 250.0 |
| 95 c.c. | 187.8 | 181.1 | 203.3 | 231.1 | 227.2 | 238.9 | 236.1 | 201.1 | 229.4 | 246.1 to 261.1 |
| Iodine value | 273.7 | 266.8 | 116.6 | 20.3 | 55.2 | 4.8 | 4.9 | 4.0 | 39.4 | 12.0 to 21.6 |
| Oil surviving polymerisation tests, % | | 4 | | | | | | | | |
| Sp. gr. | | | | | | | | | | |
| Flash-point (Abel test), °F. | 78 | 101 | 83 | 86 | 90 | 85 | 91 | 91 | 85 | 72 to 84 |

CHARACTERS OF TURPENTINE OIL AND SUBSTITUTES

| | Turpentine oil | Rosin spirit | Petroleum naphtha | Shale naphtha | Coal-tar solvent naphtha |
|---|---|---|---|---|---|
| 1. Index of ref.......... | 1.4667 to 1.4722 | 1.4701 | 1.4068 | ............ | 1.4341 |
| 2. Opt. activity......... | Active. | Variable. | None. | None. | None. |
| 3. Sp. gr.......... | 0.858 to 0.875 | 0.856 to 0.880 | 0.700 to 0.740 | 0.700 to 0.740 | 0.860 to 0.875 |
| 4. Temperature of distillation...... | 156 to 180 | Gradual rise. | Gradual rise. | Gradual rise. | Gradual rise. |
| 5. Action in the cold on coal-tar pitch. | Readily dissolves pitch to a deep brown solution. | Readily dissolves pitch to a deep brown solution. | Very slight action. | Very slight action. | Readily dissolves pitch to a deep brown solution. |
| 6. Behaviour with absolute phenol at 20. | Homogeneous mixture. | Homogeneous mixture. | No apparent solution. | Homogeneous mixture crytallising on cooling. | Homogeneous mixture. |
| 7. Behaviour on agitating 3 measures of the cold sample with 1 measure of castor oil. | Homogeneous mixture. | Homogeneous mixture. | Liquid separates into 2 layers of nearly equal volume. | Behaves like petroleum naphtha. | ............ |
| 8. Bromine absorption, dry........ | 203 to 236 | 184 to 203 | 10 to 20 | 60 to 80 | ............ |
| 9. Behaviour with sulphuric acid.. | Almost completely polymerised. | Polymerised. | Very little action. | Considerable action. | Moderate action; absorbed to form sulfonic acids. |

The following table shows the behaviour of samples of genuine American oil of turpentine when fractionally distilled in Allen's laboratory, without dephlegmator, the thermometer bulb being immersed in the liquid:

| | 1888 | 1888 | 1888 | 1899 | 1899 |
|---|---|---|---|---|---|
| Sp. gr.......................... | 0.8696 | 0.8720 | 0.8754 | 0.8662 | 0.8666 |
| Opt. rot........................ | .......... | .......... | .......... | 12.75° | 14.0° |
| Ref. ind........................ | .......... | .......... | .......... | 1.4685 | 1.4685 |
| **Fractional Distillation.** | | | | | |
| Barom. pressure in mm..... | .......... | .......... | .......... | 758 | .......... |
| First drop collected at...... | 157 | 157.5 | 157 | 155 | 155 |
| 5   % at................ | .......... | .......... | .......... | 157 | .......... |
| 10  % at................ | 158 | 158.5 | 159 | 157.5 | .......... |
| 20  % at................ | 158.5 | 159 | 160 | 158 | .......... |
| 30  % at................ | 159 | 159 | 161 | 158.5 | .......... |
| 40  % at................ | 159 | 160 | 161 | 158.5 | .......... |
| 50  % at................ | 159 | 161 | 162 | 158.5 | 156 |
| 60  % at................ | 159 | 161 | 162.5 | 159 | .......... |
| 70  % at................ | 160 | 161.5 | 164 | 160 | .......... |
| 80  % at................ | 161 | 163 | 164.5 | 161 | .......... |
| 90  % at................ | 163 | 167 | 176 | 163.5 | .......... |
| 93  % at................ | .......... | .......... | 200 | 167 | 160 |
| 96.3 % at.............. | .......... | 200 | .......... | 172 | .......... |
| 97.3 % at.............. | 200 | .......... | .......... | .......... | 165 |
| 97.5 % at.............. | .......... | .......... | .......... | 174.5 | .......... |
| Residue................ | 1.61 % thick; treacly | 2.43 % clear; treacly | 4.44 % deep brown; very viscous | 0.40 % yellowish | yellowish |
| Bromine temperature reaction. | .......... | .......... | .......... | 16.9° | 16.5° |
| Iodine value................... | .......... | .......... | .......... | 385.8 | .......... |
| Oil surviving polymerisation, %.......................... | .......... | .......... | .......... | 1.75 | 3.50 |

The following figures show the behaviour of 2 samples of *rosin spirit* of English manufacture, when 100 c.c. measure was distilled in Allen's laboratory in 1886, without dephlegmating arrangement, the thermometer being immersed in the liquid:

| | Sample A (Liverpool) | Sample B (Hull) |
|---|---|---|
| Sp. gr. at 15.5°............................. | 0.8703 | 0.8955 |
| Sp. rot. [a]ᴅ................................ | +0.87° | +12.75° |
| **Fractional Distillation.** | | |
| First drop over at......................... | 149° | 150° |
| | per cent. | per cent. |
| Distillate below 155°....................... | 4.5 | 2.0 |
| Distillate below 160°....................... | 9.5 | 4.5 |
| Distillate below 170°....................... | 19.0 | 11.0 |
| Distillate below 180°....................... | 33.5 | 18.5 |
| Distillate below 190°....................... | 57.5 | 30.5 |
| Distillate below 200°....................... | 69.5 | 41.5 |
| Distillate below 210°....................... | 74.5 | 50.0 |
| Distillate below 220°....................... | 77.5 | 57.5 |
| Distillate below 230°....................... | 81.5 | 62.0 |
| Distillate below 240°....................... | 84.0 | 65.5 |

These figures illustrate the irregularity of commercial rosin spirit. Sample B had an optical activity equal to most American oils of turpentine, but the results of the fractional distillation show that only a small proportion of true turpentine can have been present.

The analysis of turpentine oils by fractional distillation with steam has been the subject of a special investigation by W. C. Geer under
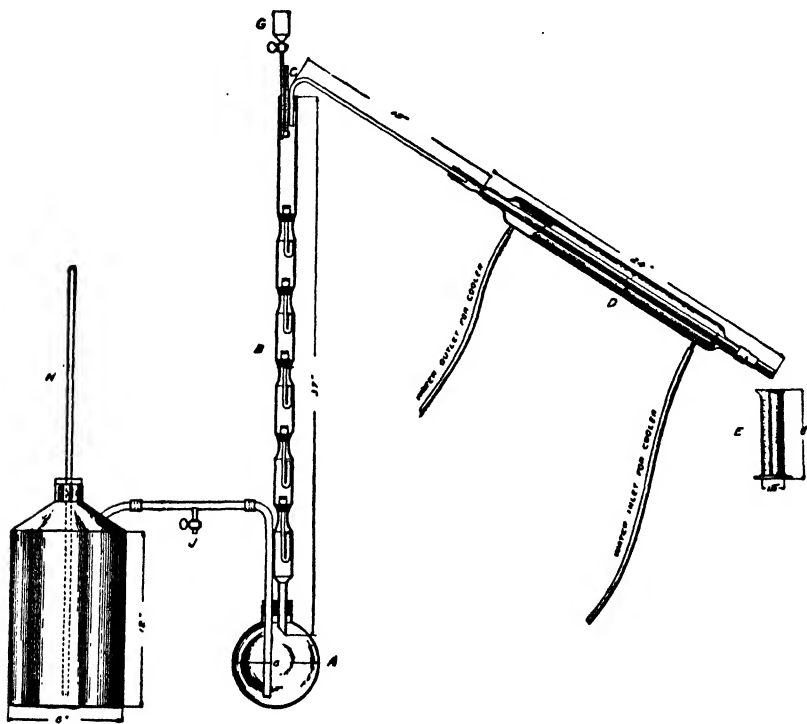


FIG. 2.—From Circular 152, Forest Service U. S. Department of Agriculture. By W. C. Geer.

the auspices of the U. S. Forestry Service. The results have been made public in Circular 152 of that Bureau. The annexed illustration (Fig. 2) shows the special form of distilling apparatus, the supporting clamps being omitted. F is the source of steam, H a safety tube, G a dropping-funnel, alongside of which is a thermometer, C. Graduated cylinders E, about 100 c.c. capacity, receive the distillates, about fifteen of which will be required. Corks may be used for

connections. The special construction of the still-head is an important feature. The foundation is an ordinary soft-glass tube about 4 cm. in diameter provided at regular intervals with constrictions, the widest being at the top. Traps are made by inserting small glass U-tubes of different lengths, supported by brass wire-gauze collars. The thistle-expansion at the top prevents the tube's falling. Each trap is about 6 mm. shorter than the one above. A strip of 40-mesh brass wire gauze about 1 cm. wide is wrapped about each tube as a collar until this is large enough to fit its particular constriction snugly. The U-tubes are then dropped into the column. It is a matter of some skill to set up the dephlegmator, but after being once adjusted it is ready for a long series of determinations. It can be cleaned after turpentine distillation by the ordinary solvents, alcohol and ether, without taking it apart. Before use, it is necessary that each of the bent tubes be filled with water, which is accomplished by pouring water slowly into the tube held upright.

To make an analysis, the boiler F is about half-filled and the funnel G entirely filled with water. The flask A is dried and weighed (to within 0.010 grm.), 500 grm. of the sample weighed into it, and connected with the condensing apparatus as shown. A sample of the original oil should be preserved for comparison with the several fractions of the distillate. The steam is then started, and when it escapes freely through the valve J, this should be closed and the burner turned down so as to give a rate of oil-distillation of about two drops per second. The burner under A should be regulated so as to prevent excessive condensation, and both burners should be surrounded by asbestos shields. The water is also allowed to drip slowly from G at the rate of about one drop per second so as to keep liquid on the brass collars.

At the beginning of the distillation it is necessary to watch the still carefully, and occasionally relieve the steam pressure through J until the dephlegmator is evenly heated and the rate of reflow uniform in each section.

In the operation the receiver is changed according to the nature of the distillation. If the temperature remains fairly constant, the receiver need be changed only rarely, but if rapid temperature changes occur, more fractions should be taken. The temperature is, of course, recorded each time the cylinder is changed. Generally

about a dozen fractions are collected. The cylinder is previously weighed dry and then after having received the fraction. The difference is the combined weight of water and oil. It is sufficiently accurate to take the volume of the water in c.c. as equivalent to its weight in grm., and the weight of distilled oil can be thus ascertained.

Geer found by using a very pure wood turpentine that in ascertaining sp. gr. of the fractions, a correction of 0.00083 should be added for every degree C. above 15° at which observation is made, and the same amount subtracted for every degree C. below.

For valuable analytic data and graphic representations of the fractionation, the original bulletin should be consulted.

The oil which distils over in a current of steam will consist of the genuine oil of turpentine, together with the more volatile portions of any adulterants, and the presence of any shale or petroleum naphtha will be indicated by the low sp. gr. of the oily portion of the distillate, after separation from the water which condenses with it.

### Specifications for American Turpentine Oil

The following specifications for American turpentine oil have been adopted by the U. S. Federal Specifications Board and the American Society for Testing Materials.

Appearance.................... Shall be clear and free from suspended matter and water.
Colour........................ Shall be "Standard"[1] or better.
Odour......................... Shall be characteristic of the variety of turpentine specified.
Sp. gr. 15.5/15.5.............. 0.862 to 0.875
Ref. ind. at 20°................ gum spirits, 1.468 to 1.478
                               wood turpentine, 1.465 to 1.478
Residue after polymerisation with 38 Normal Sulphuric acid.[2]
          Gum spirits; volume not to exceed 2.0%
          Ref. ind. at 20° not less than 1.500
          Wood turpentine; volume not to exceed 2.5%
          Ref. ind. at 20° not less than 1.480
Initial b. p. at 760 mm. pressure         150° to 160°.
Distilling below 170° at 760 mm. pressure—not less than 90%.

[1] The colour of "Standard" turpentine is such that it requires a column of liquid 50 mm. or more in length to equal the colour of a No. 1.0 yellow Lovibond glass.
[2] See page 168, for directions for preparing this acid and application of the test.

The usual commercial destructively distilled wood turpentine oil will comply with the above specifications, with the exception of the quantity distilling below 170°. In this class of oil the proportion of

dipentene and other high boiling terpenes is greater.   The manufacturers of this type of oil of turpentine advocate a maximum temperature of 180° for 90% to distil.   In order to give comparable and duplicable results, the conditions under which the distillation test are carried out must be closely controlled.

The distillation test is carried out in a standard Engler flask, as used for distilling petroleum products, having dimensions as shown in figure 3.   The type of apparatus adopted by the American Society for Testing Materials (Fig. 4) for the distillation of mineral paint thinners is preferred.   The condenser consists of a $9/16''$ OD No. 20 Stubbs gage seamless brass tube 22 inches long.   It is set at an angle of 75° from the perpendicular and is surrounded with a cooling bath 15 inches long, approximately 4 inches wide by 6 inches high.   The lower end of the condenser tube is cut off at an acute angle and curved downward for a length of 3 inches.   In case the A. S. T. M. distilling apparatus is not available, an ordinary straight glass-tube condenser, about 22 inches long, with at least 16 inches in contact with the cooling water, can be used.   The end of the condenser tube should be fitted with an adapter or should be bent down to nearly vertical position, with the tip cut off or ground down to an acute angle.   The tip should extend a short distance into the receiving cylinder.

The flask should be supported on a plate of asbestos 20 cm. square having an opening 4 cm. in diameter in the center, and heated with an open flame.   An alternative method is to support the flask in a metal cup 15 to 20 cm. in diameter, containing high boiling mineral oil or glycerine, and fitted with a concave cover having in the center a circular opening 5.5 to 6.0 cm. in diameter. The flask and burner may be surrounded by a shield to prevent fluctuation in the temperature in the neck of the flask.

The thermometer used for the distillation test in order to have the mercury column completely exposed to the hot vapours, must conform to the following specifications:

It shall be graduated from 145° to at least 200° in 0.2° intervals. Thermometers graduated above 200° may be used, provided they also comply with the following requirements: Length, bottom of thermometer to 175° mark, not more than 8 nor less than 6.5 cm. Length, top of bulb to 145° mark, not less than 1.5 cm.   Length, 145 to 175° mark, not more than 6 cm.

The thermometer shall be made of suitable thermometric glass and thoroughly annealed, so that the scale errors will not increase after continued heating.

The thermometer shall be filled above the mercury with an inert gas, with sufficient pressure above the mercury column to prevent breaking of the column. It shall have a reservoir at the top, so that the pressure will not become excessive at the highest temperature.

Every fifth graduation shall be longer than the intermediate ones, and the marks shall be numbered at each interval of $5°$. The graduation marks shall be clear-cut and fine and the numbering clear-cut and distinct.

The error at any point on the scale shall not exceed $\pm 0.5°$ when tested for total immersion of the mercury column.

**Receiving Cylinder.**—The distillate should be collected in an accurately graduated 50 or 100 c.c. cylinder. The so-called normal or precision cylinder of 50 c.c. capacity, having an internal diameter of 1.5 cm. and graduated in 0.2 c.c., is preferred. If a cylinder with larger inside diameter is used, a pasteboard cover should be placed over the top and surround the condenser tube.

**Operation.**—Place 100 c.c. of the turpentine and several small pieces of pumice (or glass) in the distilling flask, fit the thermometer so that the top of the mercury bulb is level with the bottom of the side tube, and the $175°$ C. ($347°$ F.) mark is below the cork. Place the flask in position on the asbestos board or oil bath and connect with the condenser. Apply the heat cautiously at first, and, when distillation begins, regulate the heat so that the turpentine distils at the rate of not less than 4 nor more than 5 c.c. per minute (approximately two drops per second). The initial boiling point is the thermometer reading at the instant when the first drop falls from the end of the condenser. Discontinue distillation when the temperature reaches $170.0°$ ($338°$ F.), or an equivalent thereof, depending on the atmospheric pressure, as outlined below; let the condenser drain and read the percentage distilled.

The percentage distilled below successive selected temperatures and the temperature at which each successive 10 c.c. distills may also be determined, if desired, making the necessary correction of the temperature for variations in atmospheric pressure.

**Correction for Variation in Atmospheric Pressure.**—Since distillation results are comparable only when obtained under exactly the

same pressure conditions, turpentine shall be distilled at that pressure which, at room temperature, is equivalent to a pressure of 760 mm. of mercury at 0°. Whenever the atmospheric pressure after correcting to 0° is other than 760 mm. a correction must be made. Since alteration of the pressure in the distilling system requires rather complicated apparatus, it is simpler to alter the temperature observation points to correspond to the prevailing pressure.

To determine what the atmospheric pressure at the prevailing room temperature, or at the temperature of the barometer, would be at 0°, read the barometer and thermometer alongside when about to begin distillation. Refer to table on page 163. Under the column nearest the observed pressure reading, and on the line nearest the observed temperature of the barometer will be found the correction which must be subtracted from the observed pressure reading to obtain the equivalent, or true, reading at 0°.

The distilling temperature of turpentine is affected plus (+) or minus (−) 0.057° C. for each millimeter variation of the barometer above or below the normal 760 mm. at 0° (Landolt-Börnstein, *Physikalisch-Chemische Tabellen*, Ed. 4, Table 127, p. 435). If the barometer reading, after correcting to 0°, is below 760 mm., the turpentine will distil at a slightly lower temperature than under normal pressure. Therefore, the temperature recorded at the beginning of distillation (and any others observed during the course of the distillation) must be corrected to get its equivalent at normal pressure. The final temperature observation point (170° of the specifications) must be altered accordingly to get its equivalent at the pressure (corrected to 0°) at which distillation is made.

For example, if the barometer reading, after correcting to 0°, is 750 mm., the correction of the observed initial distilling temperature will be 0.057 × 10 mm. = 0.6° approximately. If the reading of the thermometer when the turpentine begins to distil is 155.6°, the corrected initial distilling temperature will be 155.6° + 0.6° = 156.2°. Furthermore, the temperature observation point at end of distillation (170.0° at 760 mm.) must be altered to the same extent. Since the turpentine is distilling 0.6° below what it would at normal pressure, distillation must be discontinued at 0.6° below the specified limit of 170.0° to determine the percentage distilling below 170.0°.

### TABLE I.—CORRECTION TO BAROMETER READINGS[1]
[From circular F, instrument division, Weather Bureau, U. S. Department of Agriculture]

| Tempera-ture, ° | Observed reading of barometer, in millimeters | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 640 | 650 | 660 | 670 | 680 | 690 | 700 | 710 | 720 | 730 | 740 | 750 | 760 | 770 | 780 |
| 15.0 | 1.56 | 1.59 | 1.61 | 1.64 | 1.66 | 1.69 | 1.71 | 1.74 | 1.76 | 1.78 | 1.81 | 1.83 | 1.86 | 1.88 | 1.91 |
| 16.0 | 1.67 | 1.69 | 1.72 | 1.75 | 1.77 | 1.80 | 1.83 | 1.85 | 1.88 | 1.90 | 1.93 | 1.96 | 1.98 | 2.01 | 2.03 |
| 17.0 | 1.77 | 1.80 | 1.83 | 1.86 | 1.88 | 1.91 | 1.94 | 1.97 | 1.99 | 2.02 | 2.05 | 2.08 | 2.10 | 2.13 | 2.16 |
| 18.0 | 1.88 | 1.91 | 1.93 | 1.96 | 1.99 | 2.02 | 2.05 | 2.08 | 2.11 | 2.14 | 2.17 | 2.20 | 2.23 | 2.26 | 2.29 |
| 19.0 | 1.98 | 2.01 | 2.04 | 2.07 | 2.10 | 2.13 | 2.17 | 2.20 | 2.23 | 2.26 | 2.29 | 2.32 | 2.35 | 2.38 | 2.41 |
| 20.0 | 2.08 | 2.12 | 2.15 | 2.18 | 2.21 | 2.25 | 2.28 | 2.31 | 2.34 | 2.38 | 2.41 | 2.44 | 2.47 | 2.51 | 2.54 |
| 21.0 | 2.19 | 2.22 | 2.26 | 2.29 | 2.32 | 2.36 | 2.39 | 2.43 | 2.46 | 2.50 | 2.53 | 2.56 | 2.60 | 2.63 | 2.67 |
| 22.0 | 2.29 | 2.33 | 2.36 | 2.40 | 2.43 | 2.47 | 2.51 | 2.54 | 2.58 | 2.61 | 2.65 | 2.69 | 2.72 | 2.76 | 2.79 |
| 23.0 | 2.40 | 2.43 | 2.47 | 2.51 | 2.54 | 2.58 | 2.62 | 2.66 | 2.69 | 2.73 | 2.77 | 2.81 | 2.84 | 2.88 | 2.92 |
| 24.0 | 2.50 | 2.54 | 2.58 | 2.62 | 2.66 | 2.69 | 2.73 | 2.77 | 2.81 | 2.85 | 2.89 | 2.93 | 2.97 | 3.01 | 3.05 |
| 25.0 | 2.60 | 2.64 | 2.68 | 2.72 | 2.77 | 2.81 | 2.85 | 2.89 | 2.93 | 2.97 | 3.01 | 3.05 | 3.09 | 3.13 | 3.17 |
| 26.0 | 2.71 | 2.75 | 2.79 | 2.83 | 2.88 | 2.92 | 2.96 | 3.00 | 3.04 | 3.09 | 3.13 | 3.17 | 3.21 | 3.26 | 3.30 |
| 27.0 | 2.81 | 2.85 | 2.90 | 2.94 | 2.99 | 3.03 | 3.07 | 3.12 | 3.16 | 3.20 | 3.25 | 3.29 | 3.34 | 3.38 | 3.42 |
| 28.0 | 2.91 | 2.96 | 3.00 | 3.05 | 3.10 | 3.14 | 3.19 | 3.23 | 3.28 | 3.32 | 3.37 | 3.41 | 3.46 | 3.51 | 3.55 |
| 29.0 | 3.02 | 3.06 | 3.11 | 3.16 | 3.21 | 3.25 | 3.30 | 3.35 | 3.39 | 3.44 | 3.49 | 3.54 | 3.58 | 3.63 | 3.68 |
| 30.0 | 3.12 | 3.17 | 3.22 | 3.27 | 3.32 | 3.36 | 3.41 | 3.46 | 3.51 | 3.56 | 3.61 | 3.66 | 3.71 | 3.75 | 3.80 |
| 31.0 | 3.22 | 3.27 | 3.32 | 3.37 | 3.43 | 3.48 | 3.53 | 3.58 | 3.63 | 3.68 | 3.73 | 3.78 | 3.83 | 3.88 | 3.93 |
| 32.0 | 3.33 | 3.38 | 3.43 | 3.48 | 3.54 | 3.59 | 3.64 | 3.69 | 3.74 | 3.79 | 3.85 | 3.90 | 3.95 | 4.00 | 4.05 |
| 33.0 | 3.43 | 3.48 | 3.54 | 3.59 | 3.64 | 3.70 | 3.75 | 3.81 | 3.86 | 3.91 | 3.97 | 4.02 | 4.07 | 4.13 | 4.18 |

[1] These corrections apply to a mercurial barometer with brass scale. They can, however, be used for a mercurial barometer with glass scale, since the errors introduced thereby are negligible as applied to the work contemplated in this Circular. For exact correction to be applied to such a barometer see *Smithsonian Physical Tables*, p. 119; 1914. An aneroid barometer should not be relied on.

For barometer readings below 640 mm the correction can be interpolated, since the difference, at any particular temperature for each 10 mm variation in barometer reading is practically constant.

If the barometer reading corrected to 0° is above 760 mm., subtract the temperature correction from the observed thermometer reading to determine the initial distilling point, and continue distillation to 170.0° plus the correction to determine the percentage distilling below 170.0°.

## Chemical Methods of Detecting Adulterants

The usual wide difference between the price of pure turpentine oil and the cheaper mineral oils gives rise to the frequent occurrence of adulterated oil on the market.

The most usual adulterants of oil of turpentine are kerosene and certain fractions of petroleum known as "mineral spirits." "Rosin spirit," which is the more volatile portion of the product obtained by distilling ordinary rosin, is also used, but only infrequently. Certain fractions of shale oil and coal-tar are not improbable

adulterants, but their employment is not common. The table on page 155 gives a number of distinctions between real turpentine oil and its substitutes.
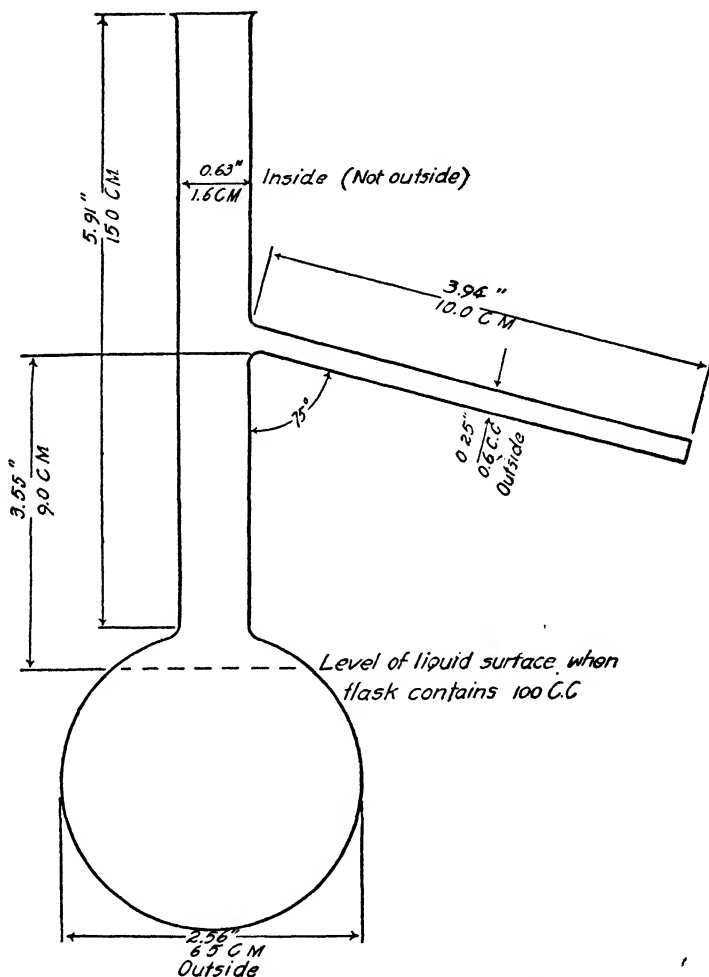


FIG. 3.—Standard 100 cc. Engler flask for distillation test on turpentine.

For the approximate estimation of petroleum naphtha in oil of turpentine and its isolation therefrom, H. E. Armstrong (*J. Soc. Chem. Ind.*, 1882, **1,** 480) recommended a process dependent on the

ready and nearly complete polymerisation of oil of turpentine by sulphuric acid, and the comparative indifference to such treatment of the paraffins which form the greater part of petroleum spirit. The method, as modified by Archbutt, is as follows: 500 c.c. of the sample of turpentine oil are placed in a stoppered bottle and treated with 120 to 170 c.c. of a mixture of 2 measures of strong sulphuric acid with 1 measure of water (2:1). The mixture is cautiously
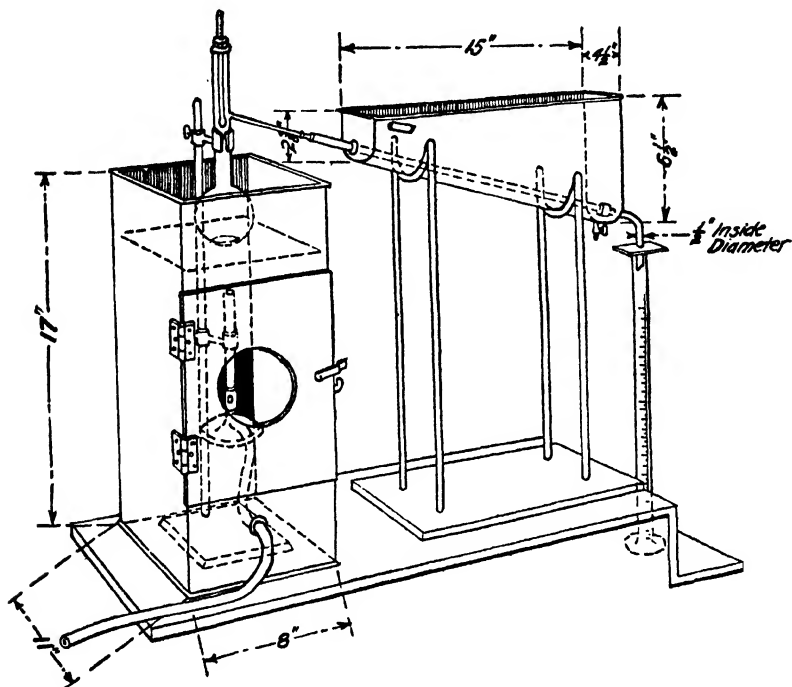


Fig. 4.—A.S.T.M. distillation apparatus.
*"Courtesy of the American Society for Testing Material."*

agitated at first, the bottle being kept thoroughly cool by a current of cold water. The turpentine is gradually converted into a viscid oil, and when this has taken place, and no more heat is developed on repeated agitation, the liquid is transferred to a separator and the acid layer tapped off. The oily layer is then transferred to a flask and subjected to steam-distillation. When all that is volatile in a current of steam has passed over, the oily portion of the distillate is separated from the aqueous layer and treated with half its volume of

sulphuric acid previously diluted with $\frac{1}{4}$ of its volume of water
(4 : 1).   The mixture is agitated as before, the acid liquid separated,
and the oily layer again distilled with steam.   When genuine turpen-
tine oil has been operated upon, the volatile product of this second
treatment consists merely of cymene and a small quantity of a



FIG. 5.

*paraffinoid hydrocarbon* ($C_{10}H_{20}$).   It never exceeds
4 or 5% of the measure of the original sample, and
with care is as low as 3%.   If the volume notably
exceeds 5% it is advisable, as a precaution, to repeat
the treatment with 4 : 1 acid.   In any case, the
residual oil should then be violently agitated with
4 times its volume of undiluted sulphuric acid at
60°, this treatment being preferably repeated.   The
residual hydrocarbon is then separated, steam-
distilled, and again measured, when the surviving
oil from pure turpentine oil, either American or
Russian, will not exceed 1.5% by measure of the
original sample.   Any excess over this proportion
represents the *minimum* admixture of *petroleum
naphtha* present.
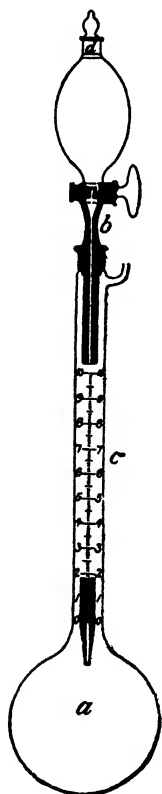
J. Marcusson and G. Winterfeld (*Chem. Zeit.*,
1909, 987) describe the following method for estima-
tion of mineral oils in turpentine:   A special appa-
ratus shown in Fig. 5 is used.   30 c.c. nitric acid (sp.
gr. 1.52) are placed in the bulb $a$ and cooled to $-10°$.
10 c.c. of the sample are placed in the stoppered
funnel and allowed to fall drop by drop into the acid,
taking about 45 minutes to introduce and frequently
agitating.   The mixture is then kept still for 15
minutes at the above-noted temperature; the stop-
pered funnel is removed, and ordinary nitric acid
cooled to $-10°$) added until the oily portion of the
liquid in the bulb is brought into the neck.   Its volume is read when
it has acquired room temperature, the bulb being meanwhile in
the freezing mixture.   The mineral oil may be removed by a pipette
and tested as usual.

A method originally proposed by A. E. Paul (*J. Ind. Eng. Chem.*
1909, **1**, 27), slightly modified, has been adopted by the Assoc.
Off. Agr. Chem. as a tentative method for the official determination

of mineral oil in turpentine oil (*J. Assoc. Off. Agr. Chem.*, 1922, 5, 552). The method is carried out as follows: 100 c.c. of the sample are distilled from a 500 c.c. Kjeldahl or other long neck flask with steam until 400 c.c. of total distillate are collected. The condenser should be sufficiently long to insure efficient condensation, and fitted with an adapter extending through a hole in a cover over the receiving cylinder.

The distillate and residue, if the latter contains any undistilled oil (neglecting any resinous deposit on the bottom of the flask) are transferred to separatory funnels, and the water drawn off. The oily portion of the distillate, returned to the distilling flask, is polymerised with 50 c.c. of conc. sulphuric acid, added slowly with constant cooling in ice water.

After thorough agitation, the temperature no longer rising, 25 c.c. water are added and the mixture again steam-distilled until 900 c.c. total distillate are recovered. A pure turpentine oil gives about 8 c.c. of oily distillate at this stage.

A volume of fuming nitric acid, (sp. gr. 1.50) equal to three times the volume of the distilled oil is placed in a bulb shape separatory funnel of about 350 c.c. capacity and cooled thoroughly in ice water. The oily distillate, combined with any oily residue from the first steam distillation, is added to the nitric acid, drop by drop, from a pipette, with continuous shaking and cooling. After the oil has all been added, the separatory funnel is fitted with a glass tube air condenser and placed in the hood until the reaction subsides. The acid is drawn off, the oily residue washed once each with fuming and with concentrated nitric acid, then several times with water.

Pure oil of turpentine gives no residue. The mineral oil recovered is from 60 to 80% of the theoretical, and has a refractive index at 20° of less than 1.500, usually about 1.450.

H. Herzfeld (*Zeit. f. öffentl. Chem.*, 1904, 9, 454) proposed a method similar to the above, but using only sulphuric acid for the polymerisations, first with concentrated, then with fuming acid. R. Böhme (*Chem. Ztg.* 1906, 30, 631) suggested a shorter procedure, replacing the two polymerisations by one, using an acid containing one part of fuming to three parts concentrated sulphuric acid. This was by far the simplest method for detecting and determining mineral oil. Vietch and Donk (*U. S. Dept. Agric. Bur. Chem. Cir.* 85) however, found that Böhme's method as published,

gave erratic results on pure oil and oils containing known small quantities of mineral oil, due to variations in the concentration of different lots of concentrated and fuming sulphuric acid. It was found that by carefully controlling the concentration of the acid used, and the method of carrying out the test, concordant and duplicable results can be obtained. The method requires fuming sulphuric acid containing 82.383% total $SO_3$, equivalent to 100.92% $H_2SO_4$. This acid has a sp. gr. at 20° of 1.846, and corresponds to 38 times normal. The allowable variation is +0.05% or −0.08% $SO_3$. The acid is prepared by mixing concentrated (sp. gr. 1.84) and fuming (50% excess $SO_3$) sulphuric acids in the ratio of 7 to 5. It is then standardised by titration against half normal alkali. From the analysis the quantity of concentrated acid (also accurately standardised) required to dilute the amount of fuming mixture on hand is determined. After addition, the mixture is again checked against standard alkali solution. For such standardisation, a quantity is accurately weighed in a weighing pipette and diluted in a volumetric flask having a volume approximately 100 times that of the pipette. This gives a solution approximately half normal. The following procedure has been adopted as official by the A.S.T.M., the U. S. Fed. Specifications Board and the A.O.A.C. It is important that the manipulation be carried out as directed.

Place 20 c.c. of the 38 N fuming sulphuric acid in a graduated narrow-necked Babcock milk-testing flask, stopper, and place in ice water to cool. Add slowly from a pipette, 5 c.c. of the turpentine. Mix the acid and turpentine, as added, by gentle shaking or rotation of the flask, keeping the temperature at about 60°–65° by continued immersion in the ice water. When the mixture no longer becomes warm on shaking, agitate thoroughly by vigorously shaking for about one-half minute. Place the flask in a water bath and heat at 60° to 65° for 10 minutes, keeping the contents of the flask thoroughly mixed by frequent vigorous shaking, no less than six times during the heating period. *Caution:* if the shaking at first is too prolonged and vigorous, there is danger of the escaping $SO_3$ forcing some of the mixture up over the mouth of the flask.

Cool to room temperature and fill the flask with conc. sulphuric acid until the surface rises well up into the graduated neck. Centrifuge for 5 minutes at 1200 revolutions per minute, or for 15 minutes at 900 revolutions per minute, or allow the flask to stand, lightly

stoppered, for 12 hours. Read the unpolymerised residue (middle of meniscus), note the consistence an colour, and determine the ref. ind. at 20°.

Pure gum spirits of turpentine with this method gives a small residue, less than 2.0%, having a straw or darker colour, viscous consistence, and a ref. ind. not less than 1.500. A limpid colourless residue with a ref. ind. less than 1.500 indicates adulteration with mineral oil. The umpolymerised residue from an adulterated oil represents from 60 to 80% of the total quantity of adulterant present.

Special precautions must be taken to prevent dilution of this acid by the absorption of atmospheric moisture. The arrangement shown in Fig. 6 is most suitable for storing and delivering measured quantities of this reagent.

With the three-way stopcocks $A$ and $B$ in the position shown, acid is siphoned into the pipette $P$, the displaced air passing into $R$. To empty the pipette, $A$ and $B$ are turned to the position shown by the broken lines, air passing in at $a$. The acid adhering to the walls of the pipette dries this air so that when it passes into $R$, on again filling the pipette, there is no accumulation of moisture in the acid remaining in the reservoir.



FIG. 6.—Acid bottle and pipette.

If such arrangement is not to be had, the acid should be kept in well-fitting glass-stoppered bottles of not more than one-half litre capacity.

The *iodine absorption* of turpentine oil is capable of furnishing valuable information. L. Archbutt, as the result of a large experi-

ence, recommends the employment of the Wijs method. Hübl solution, unless recently prepared and of full strength, does not give the maximum absorption. The time allowed for the reaction between the Wijs solution and the oil of turpentine and the temperature of the surrounding air must be exactly the same for all samples, as these factors have a great influence upon the amount of iodine absorbed. Although absorption of iodine is very rapid at first, the maximum absorption ($C_{10}H_{16} + 2I_2 = 374\%$ iodine) is not reached for many hours. This is shown by the following results communicated to Allen by Archbutt. In each experiment 0.1 grm. of oil of turpentine was used, and 30 c.c. of the Wijs solution, containing 0.7674 grm. of iodine.

| Time of action | Wijs' value of American oil of turpentine | | |
|---|---|---|---|
| | A | B | C |
| 5 minutes.................... | 277.4 | .............. | .............. |
| 10 minutes................... | 290.3 | .............. | .............. |
| 20 minutes................... | 316.1 | 324.2 | 318.7 |
| 1 hour....................... | 338.1 | .............. | .............. |
| 6 hours...................... | 359.8 | .............. | .............. |
| 18 hours..................... | 379.4 | 379.3 | 373.4 |
| 24 hours..................... | 382.6 | .............. | .............. |

Archbutt recommends 20 minutes' action as the most convenient, and states that samples of American oil of turpentine which absorb less than 320% of iodine from Wijs solution in this time should be regarded with suspicion. For the estimation, a few mg. more than 0.5 grm. of the sample is weighed into a 50 c.c. flask, which is then filled to the mark with chloroform. The solution having been well mixed, 10 c.c. are transferred to a stoppered bottle and mixed with 30 c.c. of Wijs solution containing not less than 0.7 grm. of iodine. After exactly 20 minutes' action an excess of potassium iodide solution is added and the liquid is titrated in the usual manner. At the end of the experiment, the unabsorbed iodine should be at least equal in amount to that absorbed, and not more than 5% in excess of the amount absorbed (Archbutt). If these conditions do not obtain, the test is repeated with suitably altered proportions of iodine and turpentine oil.

Many authorities recommend 1 hour's action between the turpentine and iodine solution, using the figure 340 as the minimum iodine value of a pure American turpentine oil.

The following results have been communicated by Archbutt:

| Time of action | Iodine absorption (Wijs) | | | | | | |
|---|---|---|---|---|---|---|---|
| | American turpentine oil | | | | Russian turpentine oil | | |
| | Number of samples | Highest | Lowest | Average | Number of samples | Highest | Lowest |
| 20 mins............ | 30 | 348.1 | 309.3 | 329.0 | 2 | 295.5 | 276.5 |
| 18 hours............ | 18 | 395.2 | 364.0 | 377.2 | 2 | 354.7 | 333.5 |

Utz (*Chem. Rev. Fett u. Harz Ind.*, 1905, **12,** 231) reported iodine values for various turpentine oils by the Hübl-Waller method as follows: American, average 331.6; French, 223.5 to 225.4; Austrian, 277.9; Grecian, 260.2; Russian, 181.7. He found that exposure to light for three months in the laboratory raised the iodine value of the French oil from 223 to 236, and of the Austrian oil from 277 to 345. Contrary to Utz's results, Richardson and Whitaker (*J. Soc. Chem. Ind.*, 1911, **30,** 115) report the iodine value (Hübl, 16 hrs.) for American turpentine oil as 353 to 440, while on a French oil they obtained a value of 402. A Russian oil gave an iodine value of 139, while two samples of Swedish oil gave values of 255 and 315.

The iodine value is not generally accepted as a very reliable test to determine either the purity or source of a turpentine oil.

The iodine values of various substitutes and adulterants of oil of turpentine are given on page 179. These were determined by the Hübl method.

The *bromine thermal test* was suggested by Hehner (*J. Soc. Chem. Ind.*, 1897, **16,** 87) as a substitute for the iodine value. One grm. of the oil is dissolved in chloroform, and 1 c.c. bromine added.

Each deg. rise in temperature was given as equivalent to 5.5% of iodine absorption.

A. Heiduschka (*Chem. Ztg.*, 1914, **38,** 441) suggests the use of 20 c.c. of a solution of 0.4 grm. turpentine in chloroform in a Weinhold flask, cooled to 17.5°, and addition of 1 c.c. bromine. For French turpentine the rise in temperature was 23° to 23.85°, while German

turpentine oil (probably destructively distilled) gave only 16.5° to 17.7° rise.    Rosin oil gave 13.6° rise, petroleum 2.3°, while ligroin gave only 0.85° rise.

Grimaldi and Prussia (*Chem. Ztg.*, 1913, **37**, 657) suggest the use of sulphuric acid in place of bromine.    20 c.c. of the turpentine oil are placed in a vacuum apparatus Tortelli thermoleometer, the temperature taken, and 10 c.c. of a freshly prepared reagent, made up by dissolving 1 part sulphuric acid in 7.5 parts cooled isoamyl alcohol added.    Pure turpentine oil gave a rise of 77° to 85.7°.

Destructive wood turpentine (kienöl) gave a maximum temperature rise of only 47.2°, while pinolin and rosin spirit gave a maximum of 30.1°.

W. Vaubel (*Zeit f. öffentl. Chem.* 1906, **12**, 107) has proposed the following method for determining the bromine absorption of oil of turpentine.    From 1 to 2 grm. of the oil are dissolved in chloroform, 100 c.c. water, 5 grm. of potassium bromide and 10 c.c. conc. hydrochloric acid added.    The mixture is then titrated with a standardised potassium bromate solution until the yellow colour of free bromine is observed.    The bromate solution is added gradually, at least until the coloration produced by a small addition persists for a half hour.    The bromine absorptions obtained by this method are as follows: American oil 220 to 230; French 240; based on a theoretical absorption for pinene of 254, commercial pure turpentine contains from 86 to 90% of pinene.    The presence of adulterants of turpentine would lower the values obtained perceptibly.

J. Tausz (*Chem. Ztg.* 1918, **42**, 349) has suggested a method for estimating the quantity of turpentine present in a mixture by means of the reaction with mercuric salts in the presence of methyl alcohol. Ten c.c. of the sample and also 10 c.c. of a pure turpentine check are diluted to 100 c.c. with methyl alcohol, a 10 c.c. aliquot part of each mixed with 50 c.c. of saturated mercuric chloride solution in methyl alcohol, and 50 c.c. of a N/10 solution of potassium hydroxide in methyl alcohol.    The mixtures are then diluted with 100 c.c. of water, shaken and kept in the dark for one hour.    Phenolphthalein is added, sodium chloride solution run in until a red colour develops, and the excesss KOH titrated with 0.1 normal sulphuric acid.    Each molecule of terpene present sets free a molecule of acid, which is taken up by the potassium hydroxide.    A turpentine-free control should be run at the same time.

A gravimetric modification of the above was also described. Five c.c. of the sample are diluted to 100 c.c. with methyl alcohol and 5 c.c. of this solution are mixed with 50 c.c. of a saturated aqueous solution of mercuric acetate, and heated on the water bath under a reflux condenser for 4 hours. After cooling, the precipitated mercurous acetate is collected, washed with alcohol and ether, dried, dissolved in dilute nitric acid (1:1) and precipitated with sodium chloride solution. The mercurous chloride is collected, dried, and weighed. A control test with pure turpentine oil is also made. The quantity of turpentine in the sample under examination is proportional to the quantity of mercurous chloride obtained.

Tausz also stated that when pure turpentine is heated under a reflux condenser for three hours with mercuric acetate and methyl alcohol and then steam-distilled, no trace of oil is found in the distillate. Hydrocarbons, such as cymene, cumene, petroleum spirit and mesitylene, pass over almost quantitatively.

Salvaterra (*Chem. Ztg.* 1921, **45**, 133–150) claims that Tausz's method, depending on the determination of the acid liberated by the action of mercuric chloride on turpentine oil in methyl alcohol, is untrustworthy, since the amount of acid liberated varies with the time of reaction and the origin of the turpentine oil. A method in which 20 c.c. of turpentine oil is shaken with an aqueous solution of 70 grm. of mercuric acetate in the presence of a little alcohol, followed by three hours refluxing on a steam bath, with subsequent steam distillation to recover the unchanged non-terpene adulterant, gave quite reliable results when solvent naptha, petroleum benzine and tetralin were present. Working with "kienöl," a destructive wood turpentine oil, a 10% recovery of unchanged oil which appears related to benzene was obtained. Salvaterra suggests the following somewhat modified precedure: In a litre flask place 300 c.c. water and 20 c.c. of 80% acetic acid or the equivalent of any other strength. Twenty c.c. of turpentine are added by a pipette and 51 grm. of yellow mercuric oxide added with constant shaking. Then 10 c.c. methyl alcohol are added, a reflux condenser attached and gently heated for 2 to 3 hours. On distilling with steam the unchanged hydrocarbons are recovered.

Allina and Salvaterra (*Chem. Ztg.*, 1920, **44**, 698) have proposed a method based on the fact that, when completely brominated, turpentine oil is rendered non-volatile on steam distillation.

The method is carried out as follows: In a 200 c.c. Claisen flask 20 grm. potassium bromate are dissolved in 10 c.c. water, and 20 c.c. turpentine oil added.   Hydrobromic acid (sp. gr. 1.5) is added from a burette, a little at a time, with shaking and cooling by immersion in water, until a yellow coloration persists.   Additional hydrobromic acid, to a total of 50 c.c. is then run in and the contents of the flask heated under a reflux condenser at 40° to 50° for 1 hour.

The mixture is then neutralised with sodium carbonate, decolorised with arsenic trioxide, and steam-distilled until any drops of oil coming over are found heavier than water.   Forty c.c. of distillate suffices for benzine adulteration up to 50%.   For small percentage adulteration up to 10%, 20 to 25 c.c. distillate gives practically complete recovery.   The oil is separated from the water and washed with a little fuming sulphuric acid to remove any small quantity of brominated terpene carried over.   The side tube of the flask is filled with glass wool and beads to prevent entrainment of the latter.   A burette serves well as a receiver for the distillate.

The method is not reliable when tetralin (tetra-hydronaphthalene) is present as adulterant, since the latter also takes up halogen to some extent.

In the United States the method of Veitch and Donk, page 167, is used almost exclusively for detecting and estimating the amount of adulteration of turpentine oil with mineral oil, especially in laboratories where such analyses are frequently made.   This method is simple, easy to manipulate, rapid, requires a small quantity of sample, and gives results practically as accurate quantitatively as the more cumbersome and involved methods using large amounts of expensive reagents.

The detection and estimation of small quantities of coal tar oils, such as toluene, xylene, and commercial solvent naphtha, in turpentine oils presents many more difficulties than the detection and estimation of mineral oil adulterants.

Marcusson (*Chem. Ztg.*, 1912, **36**, 413, 421) proposed the use of the method given on page 166.   He claimed that on dilution of the nitration mixture with nitric acid and pouring into 150 c.c. water, pure turpentine gave no heavy oily nitration product, but that any such product recovered represented benzol hydrocarbons.

This method has been declared unreliable by the authors of the two following methods.   Salvaterra (*Chem. Ztg.*, 1921, **45**, 151),

using the earlier method of Allina and Salvaterra, found that the large excess of hydrobromic acid also affected solvent naphtha to some extent. The large excess of bromine was necessary in view of the possible presence of destructive wood turpentine oil. He proposes to operate as follows, to give maximum recovery of solvent naphtha and, at the same time, be applicable to destructively distiled oil: In a 500 c.c. Claissen flask 12 grm. sodium bromate are dissolved in 10 c.c. of water, 20 c.c. of the turpentine oil added, and hydrobromic acid (50% sp. gr. 1.49) added, a little at a time, with shaking and cooling, until a yellow coloration persists for five minutes. The temperature is allowed to rise to 30° and maintained there for 15 minutes. The operation is preferably carried out in dim light. After neutralisation with sodium carbonate and decolorisation with arsenic trioxide, the side tube of the flask is filled with glass wool and beads and the mixture steam distilled. If wood turpentine is suspected, it is advisable to add an additional 2 c.c. of the hydrobromic acid 5 minutes before the steam distillation. The distillation is discontinued when three successive 5 c.c. of distillate do not contain more than 0.1 c.c. of oil. A total distillate of 50–60 c.c. is ample. An accuracy within 1.25% of the total theoretical amount of adulterant is claimed, except with tetralin as an adulterant. An apparatus constant, determined experimentally, is also taken into consideration when additional accuracy is desired. This is seldom practicable.

Grotlisch and Smith (*J. Ind. Eng. Chem.* 1921, **13**, 791) have described a method applicable to quite small quantities of coal tar adulterant, since the latter, on account of its odour, would rarely be used in quantity. In order to detect with certainty coal-tar oil adulteration as low as 2%, the sample is first concentrated into a smaller volume of oil. This is done by passing dry hydrogen chloride gas into 100 c.c. of turpentine oil, cooled in ice water, until it is saturated. The bottle is allowed to stand, stoppered, in a freezing mixture for about an hour, to obtain maximum crystallisation of the pinene hydrochloride. After filtration from the crystals by suction, the filtrate is distilled at reduced pressure (10 in. mercury) until 25 c.c. of distillate are recovered. This distillate is polymerised by slowly adding it, with cooling, to four times its volume of fuming sulphuric acid, containing 3 to 4% free $SO_3$. After heating at 60 to 70° on the steam bath for about 20 minutes, with frequent shaking,

the mixture is cooled and any unchanged crystalline pinene hydrochloride removed by filtration on a Hirsch funnel. The sulphonation mixture is carefully diluted with an equal quantity of water and steam-distilled. Pure turpentine oil gives not over 0.5 c.c. of a heavy, disagreeable smelling, rapidly darkening oil, having a ref. ind. at 20° above 1.500. Any mineral oil is recovered as a light faintly coloured or colourless oil with a ref. ind. below 1.500, usually 1.400.

After oil ceases to come over with the steam, the steam line is disconnected and the mouth of the flask fitted with a dropping funnel and long thermometer, extending into the liquid.

The mixture is heated to boiling, and as soon as the distillate commences to show oil, warm water is allowed to flow in from the dropping funnel at a slightly slower rate than that at which the distillate is coming off. In this way the temperature is slowly increased. Hydrolysis of the suphonic acids of the coal tar hydrocarbons takes place slowly at gradually rising temperatures, in the case of solvent naphtha beginning at about 115°. The distillation is carried on at a rate of about 3 drops per second (7–8 c.c. per minute) until frothing becomes excessive. The recovery of oil is by no means quantitative. An empirical, experimentally determined factor of 2.2 must be used to multiply the amount of oil recovered. A recovery of less than 0.5 c.c. should be neglected. The nature of the recovered oil is established by the usual nitration test, giving the heavy oily nitrobenzene homologues, with ref. ind. at 20° of 1.550 to 1.555.

The presence of benzenoid hydrocarbons in wood turpentine oil is further proved by this treatment. Authentic pure destructive wood turpentine oil gave up to 3% recovered oil from the direct distillation of the sulphonation mixture.

However, if the recovery is 4% or more, adulteration with coal tar oil is certain. The recovered oil from a wood turpentine oil is not altogether like that from a turpentine adulterated with solvent naphtha. Even steam-distilled wood turpentine gives a small residue, of about 1% on direct distillation.

The use of *rosin spirit* as an adulterant of turpentine oil is not frequent, but if used in small proportion it is difficult of detection. The odour suffices to indicate the presence of an inferior spirit, but is useless if the refined article has been employed. The behaviour on

distillation varies, but the temperature rises regularly throughout the process, and no considerable fraction is obtained at a constant temperature of 158° to 160°, as in the case of American turpentine oil. Very often there is a notable residue of viscid oil left on steam-distillation. The bromine absorption of rosin spirit is somewhat lower than that of turpentine oil, but the difference is not sufficiently marked or constant to serve as a distinction. The opt. rot. of commercial oil of turpentine is too variable to allow of the optical activity being employed for the estimation of the proportion of rosin spirit present. The reduced flash-point is perhaps the only trustworthy test for the presence of rosin spirit, after mineral oil has been shown to be absent.

According to H. E. Armstrong, the products of the distillation of rosin are always optically inactive; but this is certainly not uniformly the case with the ordinary commercial products. The sp. rot. of rosin spirit, in Allen's experience, ranges from 0° to 13°.

Evidence of the presence of *rosin spirit* is also afforded by the increased yield of hydrocarbons on treatment with 4 : 1 and concentrated sulphuric acid, as rosin spirit also yields a cymene and paraffinoid hydrocarbon on treatment with 4 : 1 acid, but no sharp estimation can be effected by the method, which would even allow a considerable proportion of the admixture to escape detection. The cymene from rosin spirit being isomeric with that from turpentine, proof of the presence of rosin spirit might possibly be obtained by examining the cymene produced.

A test for rosin spirit in turpentine oil has been described by P. H. Conradson (*J. Soc. Chem. Ind.*, 1897, **16**, 519). An aqueous solution of sulphurous acid, when shaken with rosin spirit, colours the latter yellow, the aqueous layer remaining colourless. Pure oil of turpentine, benzene, gasolene, and "160° oil," give no such coloration. After standing for several hours, the yellow obtained with rosin spirit changes on the surface to brown and further to blue, finally becoming a reddish or bluish-brown. Oil of turpentine shows no change of colour on standing with sulphurous acid solution. A snow-white emulsion is produced on shaking the mixture, and the emulsion breaks up very slowly. A sample of "wood turpentine" examined by Conradson gave the above coloration with sulphurous acid, had a specific gravity of 0.845, a flash point below 80° F., and was evidently adulterated.

**Examination for Adulteration of Turpentine Oil with Wood Turpentine:** Wood turpentine, consisting essentially of the same constituents as pure gum spirits of turpentine, is much harder to detect and identify in the latter, than the other usual adulterants especially if well rectified and present in small amount. The most marked difference is in the odour, that of the steam-distilled and destructively distilled products being distinct from each other. The physical properties are quite similar.

According to J. McCandless (*J. Amer. Chem. Soc.*, 1904, **26,** 981), adulteration with refined wood spirits (wood turpentine) may be detected as follows, after kerosene has been shown to be absent by the polymerisation process: 100 c.c. of the oil are slowly distilled with a low flame, and the refraction figure of the first 0.5 c.c. measured at 25°. In the case of genuine turpentine oil this is never below 1.4659°, usually 1.4666° to 1.4679°. Several samples of wood turpentine showed readings from 1.4640° to 1.4653°. Wood turpentines which do *not* show a low initial reading nearly always show a high reading on the final portion of the distillate. For the 97th and 98th c.c. of the distillate the reading in the case of a genuine sample never exceeds 1.4766, according to McCandless, and is usually much less, while with wood turpentine the reading may reach 1.4840.

According to R. A. Worstall (*J. Soc. Chem. Ind.*, 1904, **23,** 302), wood turpentine may be readily detected by its low iodine value, as determined with Hübl solution after 12 hours' action in the dark with a large excess of iodine. Under these conditions, Worstall found the average absorption of pure turpentine oil to be 375% of iodine, while wood turpentine gave the value 212, and a sample of turpentine oil containing even 5% of wood turpentine yielded the low figure of 360% of iodine absorbed. The figure 370 is suggested by Worstall as the minimum limit of iodine absorption for genuine turpentine oils under the above conditions.

The result of the examination of a very large number of pure and adulterated samples led Parry to consider that the behaviour of the oil toward the halogen elements gives the most useful indications of admixture with wood or stump turpentine which must be described in America either as steam-distilled or destructively distilled wood turpentine.

Both the iodine and the bromine values have been recommended in this respect, but the iodine value is, in Parry's opinion, the more

useful of the two. Its value depends on the fact that the hydrocarbons and certain other bodies present in wood turpentine—probably on account of the method of treatment adopted in its manufacture—appear to be more saturated than those present in normal turpentine, and therefore absorb less iodine to form a fully saturated compound.

The iodine value may be determined either by the Wijs or the Hübl method, the figures of course not being identical. The following processes may be used for the determination of the bromine value: (1) 1 c.c. of the oil is dissolved in 5 c.c. of chloroform, and a 3% aqueous solution of bromine added with shaking until a permanent coloration remains; the strength of the bromine solution is estimated in the usual manner, and the amount combining with the oil can be calculated. (2) 1 c.c. of the oil is dissolved in 50 c.c. of absolute alcohol, and 5 c.c. of hydrochloric acid added. A solution of 28 grm. of bromate of potassium and 100 grm. of bromide of potassium per litre is then added until a permanent brown colour remains for 1 minute after well shaking. The bromine absorbed is calculated for 1 c.c., which can be reduced to the proper bromine value by dividing it by the sp. gr., say 0.865.

Parry considers that the halogen absorption value of the 10% left after distillation of 90% of the sample affords very reliable information as regards the presence of wood turpentine, the iodine value for this fraction (Wijs) being about 355 for pure turpentine and only about 250 to 290 for wood turpentine. He gives the following figures for the various fractions of a pure and of adulterated oils and

| | (1) Pure American turpentine | (2) Wood turpentine | (3) 50% each (1) and (2) | (4) "Petroleum" turpentine | (5) 50% each (1) and (4) |
|---|---|---|---|---|---|
| Sp. gr. | 0.866 | 0.873 | 0.869 | 0.808 | 0.838 |
| Ref. ind. | 1.4720 | 1.4745 | 1.4737 | 1.4490 | 1.4610 |
| Initial boiling point | 155° | 159° | 157° | 98° | 99° |
| Distillate under 160° | 74% | 61% | 68% | 48% | 62% |
| Distillate under 170° | 94% | 78% | 84% | 74% | 82% |
| Bromine value | 2.2 | 1.46 | 1.82 | 0.05 | 1.1 |
| Iodine value (Hübl) | 372 | 264 | 321 | 9.0 | 190.5 |
| Iodine value (Wijs) | 350 | 240 | 298 | 8.4 | 179 |
| Iodine value of last 10% residue (Hübl) | 360 | 251 | 304 | 9.0 | 184 |
| Iodine value of last 10% residue (Wijs) | 355 | 242 | 298 | 8.5 | 177 |
| Ref. index of first 20% | 1.4719 | 1.4731 | 1.4728 | 1.448 | 1.4660 |
| Ref. index of second 20% | 1.4700 | 1.4730 | 1.4720 | 1.449 | 1.4675 |
| Ref. index of third 20% | 1.4712 | 1.4734 | 1.4722 | 1.4481 | 1.4721 |
| Ref. index of fourth 20% | 1.4712 | 1.4732 | 1.4721 | 1.4470 | 1.4721 |
| Ref. index of fifth 20% | 1.4781 | 1.4842 | 1.4821 | 1.4495 | 1.4735 |

proposes the following limits for the characters of genuine American turpentine oil:

| | |
|---|---|
| Sp. gr. at 15°........................................ | 0.862 –0.870 |
| Ref. index.......................................... | 1.4680–1.4730 |
| Initial b. p......................................... | 154°–155.5° |
| Distillate under 160°................................ | 72–74.5% |
| Distillate under 170°................................ | 95–97.5% |
| Bromine value...................................... | 1.96–2.31 |
| Iodine value (Hübl)................................. | 360–375 |
| Iodine value (Wijs)................................. | 335–350 |
| Iodine value of last 10% residue (Hübl)............ | 349–369 |
| Iodine value of last 10% residue (Wijs)............ | 350–365 |
| Ref. ind. of first 20%.............................. | 1.4700–1.472 |
| Ref. ind. of second 20%............................ | 1.4700–1.4724 |
| Ref. ind. of third 20%............................. | 1.4710–1.4735 |
| Ref. ind. of fourth 20%............................ | 1.4710–1.4740 |
| Ref. ind. of fifth 20%.............................. | 1.4780–1.4821 |

See also U. S. Govt. specifications for Turpentine Oil, page 159.

When highly refined steam distilled wood turpentine is used as adulterant in amounts up to 15 or 20%, the distinctive odour can usually be distinguished. When present in smaller amount the odour is frequently not noticeable. When 100 c.c. of the oil are carefully distilled from a Ladenburg flask, which gives a fair degree of fractionation without excessive heating, as would be necessary were a longer fractionating column used, the last 10 c.c. distilling from 165° to 170°, or better the final 5 c.c. may be used to determine the presence of wood turpentine. If as much as 10% are present, the characteristic "piney" pine oil odour is obtained. The iodine value of this fraction should be determined.

*Miscellaneous Tests.*—Utz (*Chem. Zentralbl.*, 1905, 1, 1673) proposes to identify kienöl by the use of Bettendorf's reagent. This is a freshly prepared saturated solution of pure stannous chloride in concentrated hydrochloric acid. Equal parts of the oil and the reagent are shaken together. With pure gum spirits of turpentine (Austrian, Grecian and American) the reagent is coloured yellow to orange, and the oil is colourless to yellow. With destructive wood turpentine present, the reagent is coloured from a raspberry red to a blood red, with the oil also sometimes coloured.

The Halphen colophony test may also serve to throw light on the quality of the oil under examination. A little of the oil, dissolved in a solution of one part phenol and two parts carbon tetrachloride,

is subjected to the action of bromine vapours, given off by a solution of one part bromine in two parts carbon tetrachloride. Pure turpentine gives only brown tones. If destructive wood turpentine or rosin spirits are present, the solution takes on a wine red to violet colour. If rosin is present, the first colour tone is bluish, changing to violet under the continued action of the bromine.

Pure gum spirits of turpentine, if fresh, should give only a pale yellow coloration on shaking equal parts of the oil and concentrated hydrochloric acid. The development of a brown or red colour, at once or after standing for five minutes, indicates either oxidation due to exposure to air and light, or the presence of wood turpentine oil. The test is not at all conclusive, and should be used only to serve as a guide to further tests.

The German law requires that oil of turpentine employed for the denaturation of alcohol shall have the following characters: Sp., gr., between 0.855 and 0.865 at 15°. When 100 c.c. measure is fractionally distilled in a metal flask furnished with a dephlegmator, not more than 5 c.c. must come over below 150°, but at least 90 c.c. at 160° When 20 c.c. of the sample are shaken vigorously with an equal volume of water, and the liquid allowed to stand till clear, the upper (turpentine) stratum must measure at least 19 c.c.

A. and P. Andourad (*J. Pharm. Chim.* [6], 1902, **15,** 99) described a petroleum product from America, known as "white spirit," which is much used in France for the adulteration of oil of turpentine. "White spirit" has a violet-blue fluorescence, and a sp. gr. of 0.807. It is almost optically inactive, and begins to distil between 150° and 160°, the last fractions having a high b. p. It leaves about 40% of residue at 205°.

Banner's "*turpentine substitute*," according to the specification (Brit. Patent, 1885, 12249), is essentially prepared by selecting, during the distillation of petroleum, coal oil, or other similar heavy hydrocarbons, groups of fractions containing hydrocarbons of a sp. gr. ranging from 0.730 to 0.840. The characters of 6 samples examined by Archbutt are given in the table on page 154 under the heading "Patent Turpentine."

**Terebene,** according to the B. P. and U. S. P., is a mixture of dipentene, and other hydrocarbons, obtained by agitating oil of turpentine with excessive quantities of sulphuric acid until it no longer possesses optical activity. The product is then distilled with steam. Some

manufacturers of terebene do not carry the process sufficiently far to produce a totally optically inactive product.

Terebene is a colourless liquid with an agreeable thyme-like odour and an aromatic terebinthinate taste. It is only slightly soluble in water, but dissolves in 3 vols. of 90% alcohol. On exposure to air and light, terebene gradually resinifies, becoming yellowish and acid. The sp. gr. of terebene ranges from 0.862 to 0.866 at 15.5°. Terebene should be optically inactive. The British Pharmacopœia requires that terebene should not contain more than 15% of constituents distilling below 165°, and that all except a slight viscid residue should distil between 156° and 180 (absence of excess of resin). According to the United States Pharmacopœia (8th Rev.), terebene distils between 155° and 165°. Terebene should not redden moist blue litmus-paper, and should yield only a very slight non-volatile resinous residue on evaporating 10 c.c. in an open dish at 100°.

Tyrer and Wertheimer (*Pharm. J.* [4], 1900, **11**, 101) find that, with due precautions, American oil of turpentine yields terebene answering the official requirements, except in the respects that 5% remains undistilled at 180°, and that no fraction is absolutely devoid of optical activity. 2 samples of "terebene" examined by these observers boiled considerably above the official limits, and had thus been distilled by steam under pressure or by a direct flame. Terebene from French oil of turpentine was found, on fractional distillation, to yield 28% of a mixture of optically-inactive substances.

### Wormseed Oil (Levant Wormseed Oil)

This oil should not be confused with the oil of "American wormseed," which is in reality chenopodium oil. Levant wormseed oil is usually from the unexpanded flower-buds of *Artemisia maritima*, but, according to Parry, other species probably contribute.

The true wormseed oil is a thick yellow or brownish oil, having the camphoraceous odour of cineole. It has a sp. gr. of 0.930 to 0.935. These figures represent the usual limits of sp. gr. The outside limits, as given by Gildemeister and Hoffman (*The Volatile Oils*), are 0.915 to 0.940. The oil is slightly lævorotatory. When rectified, it is colourless.

The constituents, so far as known, are cineole, $\alpha$-terpineol, terpinenol, terpinene, pinene and, possibly, dipentene.

## Wormwood Oil (Oil of Absinthe)

This oil is obtained by the distillation of the green herb *Artemisia absinthium*, which is extensively cultivated in North America. It is often called absinthe oil.

Wormwood oil is dark green or greenish-blue, and has a strong odour and acrid taste. Its sp. gr. ranges from 0.925 to 0.955.

Miller, (*Bull. Univ. Wis.* 693) gives, for the examination of 6 typical samples of Wisconsin oil, figures which do not indicate so great a variation. Adulteration with oil of turpentine may, therefore, be inferred from lowered sp. gr. Since wormwood oil contains only slight traces of pinene, the presence of turpentine in the oil may also be detected by the characters of the first 10% of the distillate. The distillate from pure oil dissolves in 2 vols. of 80% alcohol to a clear solution. Very small additions of turpentine oil, which is sometimes an adulterant of this oil, may thus be detected. The opt. rot. of the oil cannot well be taken, owing to its deep colour, but since the chief constituent, thujone, is strongly dextrorotatory, the oil will no doubt be optically active in this direction.

The principal constituent is a ketone, thujone (see page 564). Thujyl alcohol is also present to a considerable extent, as well as thujyl esters of acetic, isovaleric, and palmitic acids. Phellandrene is present to a very small extent, pinene only in slight traces, cadinene and azulene.

A sample of the pure oil examined by Schimmel & Co. was found (upon acetylation and saponification) to yield 24.2% of thujyl alcohol, of which 13.9% was present in the form of esters (equivalent to 17.6% of thujyl acetate).

**Japanese wormwood oil** (Yomugi oil), from *Artemisia vulgaris*, is bright green and has a marked odour of cineole, which it contains, and probably also thujone, Schimmel & Co. found it to have the following characters: Sp. gr. 0.9101; opt. rot., −13.25°; acid value, 1.56; ester value, 29.81. The oil was not completely soluble in alcohol.

## Wintergreen Oil

True wintergreen oil is the product of the distillation of the leaves of *Gaultheria procumbens*, but the oil from the bark of *Betula lenta* is

so closely identical with it that the two are used more or less indifferently, except in so far as the latter is much less expensive than the former, and so finds a larger employment. Both oils consist almost entirely of methyl salicylate, their characters being as follows:

|  | Gaultheria oil | Betula oil |
|---|---|---|
| Sp. gr.......................... | 1.180–1.187 | 1.180–1.187 |
| Ref. index..................... | 1.5350 | 1.5350 |
| Distils between................ | 218°–221° | 218°–221° |
| Rotation......:............... | under–1° | 0° |
| Methyl salicylate.............. | 98–99% | 98–99% |

The principal adulterant is synthetic methyl salicylate.

Although numerous colour tests have been proposed to distinguish between oil of wintergreen, oil of sweet birch and artificial methyl salicylate, all of them have proved to be of small importance in practical use.

If traces of chlorine are found in the oil (see under Oil of Almonds) a crude artificial methyl salicylate must have been used as the adulterant.

## Ylang-ylang Oil

The tree whose flowers yield this much valued oil is *Cananga odorata*, which grows to perfection in the Phillippine Islands, more especially in Manila. The oil produced in Java and the neighbourhood is of far less value and is known as Cananga oil. The reason for the difference between these two commercial varieties is still doubtful, as there is every reason to believe that the tree is identical in both cases.

The constituents of the oil so far identified are as follows: linalol, geraniol, cadinene, *para*cresol methyl ether, benzoic and acetic esters, pinene, eugenol methyl ether, isoeugenol, methyl salicylate, and benzyl esters. Formic acid esters, safrol, isosafrol, nerol and farnesol are also probably present in the oil.

The physical characters of the oil vary within very wide limits and organoleptic tests are very necessary in its valuation. The oils have the following characters:

|                                   | Manila        | Madagascar    | Bourbon       |
| --------------------------------- | ------------- | ------------- | ------------- |
| Sp. gr.                           | 0.922–0.970   | 0.960–0.981   | 0.960–0.975   |
| Rotation                          | −27° to −52°  | −30° to −42°  | −35° to −43°  |
| Ref. ind.                         | 1.491–1.506   | 1.496–1.513   | 1.499–1.515   |
| Ester value.                      | 75–155        | 110–175       | 131–162       |
| Non-volatile (2 hours at 100°).   | 4–16.5%       | 15–30%        | 22–43%        |

## Cananga Oils

Sp. gr. ................................... 0.900–0.950
Rotation .................................. −17° to −55°
Ref. ind. ................................. 1.4950–1.5110
Ester value ............................... 30–100

These oils should be soluble, with at most slight opalescence, in 0.5 to 2 volumes of 90% alcohol, becoming turbid by further addition of alcohol. Petroleum oil is a common adulterant of cananga oil and will, apart from altering the physical character above quoted, decrease the solubility. Benzyl benzoate will be indicated by a high fixed residue on the water-bath after 2 hours' heating.

Turpentine, alcohol and also cocoanut oil have been used as adulterants of this oil.

In a communication to the *Philippine J. Sci.*, in 1908, R. F. Bacon, who has studied the production of ylang-ylang oil in Manila in much detail, and has himself superintended the distillation of certain of the samples upon which he reports, gave as the figures from his examinations the following:

|                          | FIRST QUALITY   | SECOND QUALITY  |
| ------------------------ | --------------- | --------------- |
| Sp. gr. 30°/40°.         | 0.911–0.958     | 0.896–0.942     |
| Optical rotation (30°).  | −27° to −49°    | −27° to −87°    |
| Ref. index (30°).        | 1.4747–1.4940   | 1.4788–1.5082   |
| Ester value.             | 90–138          | 42–94           |

At a later date, in a communication to the same journal he confirmed his classification, and presented figures for the examination of a further number of oils. He gave as limits for first and second grade oils the following:

|                                | FIRST QUALITY                        | SECOND QUALITY                          |
| ------------------------------ | ------------------------------------ | --------------------------------------- |
| Sp. gr. 30°/40°.               | 0.910–0.945 (mostly 0.920–0.930)     | 0.905—0.0925 (mostly 0.910–0.915)       |
| Opt. rot.                      | −22° to −50° (mostly −40° to −50°)   | −38° to 79° (very irregular)            |
| Ref. ind.                      | 1.4863–1.4944                        | 1.4910–1.5030                           |
| Ester value.                   | 92–129 (average 104)                 | 71–88 (average 81)                      |
| Ester value after acetylation. | 154–214 (average 182)                | 96–141 (average 118)                    |

## Terpeneless Essential Oils

By subjecting the essential oils to careful distillation under reduced pressure, there are obtained as distinct fractions, the hydrocarbons or terpenes of the oils, and an odorous oxygenated portion, which can be kept behind in the distillation apparatus. The terpene fraction has comparatively little or no odour in most cases; while, as a rule, the oxygenated or high-boiling fraction retains all the good qualities of the original oil in a heightened degree. In other words, the oil has been concentrated, and the residual valuable fraction is found to have a far greater solubility coefficient (in alcohol) than the original oil, a fact which is of considerable commercial importance. In certain cases, distillation, at however low a pressure, would cause decomposition of the valuable oxygenated constituents of the oil. When this is the case, the terpeneless oil is of very little value, since it does not represent the unaltered concentrated oil. Some few oils contain so little terpene that the terpeneless oil possesses little advantage over the natural product.

The chief constituents of essential oils, prepared in a pure state (*e. g.*, citral, eugenol, safrol, etc.) have occasionally been termed terpeneless oils, but this is manifestly a misnomer. In many cases these products are inferior to the real terpeneless oils, though sometimes they are superior to them. The 2 classes should, however, be carefully differentiated and the term " terpeneless oil " restricted to the product properly coming under that description.

Völckel and Schweitzer in 1840, and Haensel in 1876, first pointed out the value of this procedure. Many other observers followed up their researches, and the increased usefulness of the terpeneless products has been widely recognised. The terpenes as a class readily oxidise and resinify on exposure to air, and at the same time develop an unpleasant odour and taste. Essential oils, which are thus liable to lose their delicate odour and flavour on keeping, may therefore frequently be stored in a terpeneless state for a long time without deterioration. Thus the terpeneless oils are specially valuable in the manufacture of perfumes, liquors and essences, and for medicinal purposes.

The following table shows the physical characters of many of the best-known terpeneless oils. The data are chiefly due to C. T. Bennett and to Hollands Distillery of essential oils—Ltd., through the *Perfumer and Essential Oil Record* (1923).

## CONCENTRATED OR TERPENELESS OILS

| | Concentration | Specific gravity | Opt. rot. | Ref. ind. (25°) | Solubility in alcohol | |
|---|---|---|---|---|---|---|
| Angelica.............. | 20 | .975– .980 | − 1° to + 1° | ............ | ........... | |
| Anise................ | 1½ | .982– .984 | 0° to − 1° | 1.553–1.554 | 1 in 1 | (90%) |
| Bay................. | 2 | 1.025–1.045 | 0° to − 1° | 1.526–1.528 | 1 in 2 | (70%) |
| Bergamot............ | 2½ | .885– .890 | − 6° to −10° | 1.455–1.457 | 1 in 1 | (80%) |
| Calamus............. | 3 | .900– .915 | − 8° to −20° | ............ | ........... | |
| Cananga............ | 5 | .900– .915 | − 8° to −20° | 1.486–1.488 | 1 in 1 | (95%) |
| Cardamoms.......... | 2 | .943– .956 | +33° to +46° | ............ | ........... | |
| Caraway............. | 2 | .960– .964 | +58° to +60° | 1.495–1.497 | 1 in 2 | (70%) |
| Celery.............. | 8 | 1.015–1.080 | −40° to −60° | 1.500–1.505 | 1 in 2 | (85%) |
| Citronella (Ceylon)... | 2 | .910– .930 | − 2° to − 5° | ............ | 1 in 2 | (70%) |
| Citronella (Java)..... | 1½ | .880– .900 | − 1° to 1° | 1.470–1.472 | 1 in 2 | (70%) |
| Cloves.............. | 1½ | 1.060–1.070 | Nil | 1.534–1.538 | 1 in 3 | (60%) |
| Coriander........... | 1½ | .877– .881 | + 8° to +10° | 1.463–1.465 | 1 in 3 | (65%) |
| Cummin............. | ...... | .965– .975 | + 4° to + 8° | ............ | ........... | |
| Dill................ | 2 | .960– .965 | +52° to +62° | 1.488–1.489 | 1 in 1.5 | (75%) |
| Galangal............ | ...... | .940– .950 | − 3° to − 3° | ............ | ........... | |
| Ginger.............. | 10 | .880– .890 | +10° to +28° | 1.471–1.486 | 1 in 1 | (90%) |
| Hops............... | 8 | .935– .950 | − 1° to + 1° | ............ | ........... | |
| Juniper............. | 5 | .935– .965 | − 4° to + 4° | 1.500–1.508 | 1 in 1 | (90%) |
| Lavender............ | 2½ | .895– .905 | − 7° to − 9° | 1.458–1.460 | 1 in 2 | (70%) |
| Lemon.............. | 20 | .893– .899 | − 5° to − 9° | 1.477–1.481 | 1 in 1 | (80%) |
| Lemon (Sesquiter-peneless)........... | 25 | .900– .905 | 0° to − 3° | 1.477–1.481 | 1 in 3 | (70%) |
| Limes............... | 15 | .918– .925 | − 1° to − 6° | 1.479–1.481 | 1 in 1 | (80%) |
| Neroli.............. | 2 | .885– .890 | + 2° to + 6° | ............ | 1 in 3 | (70%) |
| Nutmeg............. | 5 | 1.010–1.100 | 0° to + 6° | 1.505–1.516 | 1 in 2 | (80%) |
| Orange (sweet)....... | 50 | .885– .895 | + 8° to +25° | 1.465–1.474 | 1 in 1 | (80%) |
| Orange (Sesquiter-peneless)........... | 65 | .900– .905 | + 3° to + 6° | 1.465–1.477 | 1 in 3 | (70%) |
| Peppermint.......... | 1½ | .905– .915 | −24° to −30° | 1.458–1.460 | 1 in 3 | (70%) |
| Petitgrain........... | 2 | .890– .895 | + 1° to + 3° | 1.459–1.461 | 1 in 1 | (80%) |
| Pimento... ......... | 1½ | 1.056–1.064 | Nil | 1.535–1.537 | 1 in 1 | (70%) |
| Rose (stearopteneless) | 1½ | .882– .885 | − 3° to − 5° | 1.466–1.468 | 1 in 1 | (70%) |
| Rose-geranium....... | 1½ | .890– .895 | − 7° to −11° | 1.463–1.465 | 1 in 2 | (70%) |
| Rosemary............ | 5 | .925– .960 | 0° to +10° | 1.470–1.462 | 1 in 2 | (75%) |
| Sage................ | 6 | .930– .940 | 5° to +10° | 1.465–1.467 | 1 in 2 | (75%) |
| Spearmint........... | 4 | .950– .964 | −40° to −50° | 1.488–1.490 | 1 in 2 | (75%) |

## TABLE
## OF CHARACTERS AND CONSTITUENTS OF THE BETTER
## KNOWN ESSENTIAL OILS

The following tabular list of the characters of the better known essential oils was prepared originally for the 3d ed. of this work, at the request of Allen, by A. R. Tankard and John Evans. Leffmann and LaWall revised the table in the 4th edition, and Nelson and Russell have further revised it in this edition.

The data given have been compiled from E. J. Parry, Chemistry *of Essential Oils* (4th ed.); Gildemeister and Hoffmann, The *Volatile Oils* (2nd ed.); various technical reports and the current literature. The limits given in the instance of official oils do not necessarily conform to the Pharmacopœial standards, but are those found for authentic samples.

## TABLE OF ESSENTIAL OILS

| Oil | Chief sources | Sp. gr. at 15° | Opt. rot.° | Other characters | Known constituents |
|---|---|---|---|---|---|
| Acacia........... | Flowers of *Acacia cavenia*. | ................. | ................. | ................. | Eugenol (40 to 50%); methyl-eugenol (8%); methyl-salicylate (20%); benzyl alcohol (20%); benzaldehyde; geraniol; anisic aldehyde; and probably also limalol, decyl aldehyde, and ionone. |
|  | Flowers of *Acacia farnesiana*. | 1.0475 to 1.0575 |  | Ref. ind. 1.5133 to 1.5150 | Similar to above, but eugenol is absent. |
| Achillea (see also *Iva Oil*). | Flowering herb of *achillea coronopifolia* | 0.924 | ................. | A deep blue oil, with an odour of tansy. |  |
|  | Herb of *A. nobilis*... | 0.905–0.915 | −10.7 | Camphoraceous odour and bitter taste. Ref. ind. 1.4455. | Camphene, borneol and esters. |
|  |  | 0.936 |  | Distils at 170°–265°...... |  |
| Ajowan........... | Fruit of *Carum ajowan.* (Carum.) S. & Co. | 0.910–0.930 | +1.0 to +5 | Ref. ind. 1.498 to 1.5005 | Thymol, 40–50%; cymene, α-pinene, dipentene; γ-terpinene. |
|  | Herb of *carum ajowan* | 0.900–0.930 0.860 | +0.7 | A light brown oil, sol. in 6 parts 90% alcohol, with separation of a paraffin. | Thymol (about 1%); phellandrene (trace). |
| Allspice.......... | (See *Pimento Oil*.) |  |  |  |  |
| Almond oil (bitter) | Fruit of *amygdalus communis, var. amara.* | 1.045–1.171 | Inactive | Ref. ind. 1.532 to 1.544 | Benzaldehyde, $C_6H_5COH$, over 90%. Hydrocyanic acid 2 to 4%. |
| Ambrette......... | *Hibiscus abelmoschus* | 0.900–0.905 0.9145 | up to +13° | Congeals at 10°. Deposits a paraffinoid hydrocarbon. | Farnesol, palmitic acid. |
| Ammoniacum...... | The gum-resin from the stem of *Dorema ammoniacum.* | 0.885 to 0.894 | +1 to +3 | Distils between 250° and 290° Ref. ind. 1.4923 to 1.4808 | Linalyl acetate, citronellyl acetate, ferulene, doremone. doremyl acetate, acetyl alcohol. |

| | | | | | |
|---|---|---|---|---|---|
| Angelica.......... | Root of *Angelica officinalis.* | 0.855–0.905 / 0.8925 | +18.0 to +36.0 / 15.0 | Turns yellow on exposure to light. Saponification value, 37.7. Distils chiefly between 60°–70°. | Phellandrene; methylethyl acetic acid; oxymyristic acid. |
| Japanese.......... | Fruit of *A. officinalis.* Root of *A. refracta* and *Angelica anomala.* | 0.856–0.890 / 0.905+0.915 | +10 to +13 | Pale yellow; darkens in colour with age. At 10°, crystals of a fatty acid separate melting at 62°–63°. Oil distils between 170°–300°. | Phellandrene; methyethyl acetic acid; oxymyristic acid. |
| Angostura......... | Bark of *Galipea cusparia.* | 0.928–0.960 | −7 to −50 | 1.5074 | Cadinene; galipol, $C_{15}H_{26}O$, 14%; galipene; an oxygenated body; pinene, cadinene. |
| Anise............. | Fruit of *Pimpinella anisum.* | 0.975–0.990 | −1 to −3 | At 15°–19° solidifies to a white, crystalline mass (anethol). B. p. 234°. Ref. index, 1.594 to 1.5760. | Methyl-chavicol; about 90% anethole; anise-ketone. |
| Anise............. | Bark from Madagascar. Botanical origin uncertain. | 0.969 | −0.8 | ................. | Methyl-chavicol; small amount of anethole. |
| Anise, Star (Chinese) [Badiana oil]. | Fruit of *Illicium verum* | 0.980–0.990 | 0 to −3 | At 12–18° solidifies. Ref. ind., 1.552 to 1.558. | Anethole; anise aldehyde and ketone; anisic acid; methyl-chavicol; pinene; phellandrene; safrole; ethyl-ether of hydroquinone. |
| Anise, Star (Japanese) [Badiana oil]. | Fruit of *Illicium religiosum.* | 0.984 to 0.985 | −4.1 | Sol. in 5 to 6 vols. 80% alc. with sep of paraffin. | Anethole; safrol; eugenol; a terpene (limonene?). |
| Apopin (Shu-yu).. | From one of the *Lauraceæ.* | 0.870 to 0.8952 | −1 to −16 | ................. | Camphor; eugenol; safrol; cineole; dipentene, pinene, formaldehyde, linalol. |
| Arnica............ | Root of *Arnica montana.* | 0.980–1.000 | −2.0 to +1 | Yellow colour, becoming darker with age. | Dimethyl ether of thymohydroquinone, (80%); phlorol iso-butyrate, (20%); a very little phloral dimethyl-ether. |

## TABLE OF ESSENTIAL OILS—Continued

| Oil | Chief sources | Sp. gr. at 15° | Opt. rot.,° | Other characters | Known constituents |
|---|---|---|---|---|---|
| Artemisia......... | Herb of *Artemisia glacialis* (so-called *Genepi des Alpes*). Herb of *Artemisia vulgaris* (common mugwort). | 0.964 to 0.970 <br> 0.907; 0.939 | .............. <br> −8 to −19 | Distils at 195–310°. Solidifies at 0° to a buttery mass. <br> Ref. ind. 1.4976 to 1.4855. | Cineole, a fatty acid, m. p. 61°. <br> Alpha-thujone. |
| Asafœtida........ | The gum-resin from root of *Ferula fœtida*, etc. | 0.915 to 0.993 | +11 to −36 | Ref. ind. 1.494 to 1.526. | Pinene (?); a substance containing $C_{10}H_{16}O$; the sulphuretted substances; $C_7H_{14}S_2$; $C_8H_{14}S_2$; $C_{10}H_{16}S_2$; a blue fraction. |
| Asarum Canadense | Rhizome and root of *Asarum Canadense* ("Canada snake-root"). | 0.951–0.952 | −10.5 to −22 | Yellowish-brown oil. Ref. ind. 1.4854 to 1.4899. | Dextro- and lævopinene, 2%; alcohols, including geraniol, 35%; methyl-eugenol, 37%; l-terpineol, borneol, linalol and a deep blue fraction. |
| Asarum Euro-pæum. | Rhizome and root of *Asarum Europæum* ("Asara-bacca"). | 1.015–1.070 | .............. | Thick, brownish liquid. | Pinene; methyl-eugenol; asarone; a blue fraction. |
| Backhousia citriodora. | Leaves of *B. citriodora*. | 0.895 to 0.900 | Inactive or slightly −. | Ref. ind. 1.486 to 1.4890. Distils 215°–230°. | Aldehydes, 95% (chiefly citral); sesquiterpenes (traces). |
| Badiana.......... | (See *Anise Oils*.) | | | | |
| Balsam-fir........ | Leaves of *Abies balsamea*. | 0.862 to 0.865 | −25 to −38 | Ref. ind. 1.4730 to 1.4765. | Pinene |
| Basil (Basilicum).. | Fresh herb of *Ocymum basilicum*. | 0.900 to 0.930 | −6 to −22 | .............. | Pinene; cineole; camphor; linalol; methyl-chavicol; eugenol. |
| Bay (Myrcia)...... | Leaves of *Pimenta acris*. | 0.965–0.985 <br> 0.965–0.995 | 0 to −2° <br> Up to −2. | Ref. ind. 1.509 to 1.520. Ref. ind. 1.487 to 1.585. | Eugenol and chavicol (60–65%); methyl-chavicol; methyl-eugenol; citral; myrcene; l-phellandrene. |
| Californian. | Leaves of *Umbellularia California*. | 0.930 to 0.950 | −22 to −25 | Ref. ind. 1.4785. | Cineole; eugenol, pinene, umbellulone, safrol, methyl-eugenol. |

| | Source | Sp. gr. | Rotation | Properties | Constituents |
|---|---|---|---|---|---|
| Bergamot | Fresh fruit of *Citrus bergamia* (by expression). | 0.882–0.886 | +8 to +22 | Greenish or greenish-yellow liquid. Begins to distil at about 170°. Ref. index 1.465 to 1.470. | Limonene; dipentene; linalol; linalyl acetate (36–39 %). *l*-camphene bisabolene dihydrocuminic alcohol, nerol, terpineol. |
| Betle | Leaves of *Piper betle.* | | | | Beta-phenol (para-eugenol); cadinene; sometimes chavicol. |
| | Dried leaves from Siam. | 1.024 | | | |
| | Fresh leaves from Manila. | 1.044 | | | |
| | Fresh leaves from Java. | 0.958 | −1.75 to +2.8 | | |
| Boldo | Leaves of *Peumus boldus.* | 0.915 to 0.960 | −2° to +1° | Ref. ind. 1.4708. Distils 175°–250°. | Para-cymene, cineole, ascaridole. |
| Boronia | *Boronia polygalifolia.* | 0.839 | +10 | Sweet odour resembling tarragon and rue. Distils largely between 150° and 190°. | |
| Buchu | Leaves of *Barosma serratifolia.* | 0.918 to 0.961 | −12 to −36 | Strong, mint-like odour. | Diosphenol (small amount); limonene; dipentene; menthone. |
| | Leaves of *B. betulina.* | 0.935 to 0.970 | −15 to −48 | The sp. gr. given refers to that of the oil after the diosphenol had separated at ordinary temperature. | Diosphenol (large amount); otherwise like above oil. |
| | Leaves of *B. crenulata* | 0.936 | −15.3 | | Diosphenol (small amount) otherwise like above oil. |
| Cajuput | Leaves of *Melaleuca leucadendron.* | 0.917–0.930 | 0 to −4 | When crude, is a bluish-green liquid with a camphoraceous odour and somewhat bitter taste. Green colour usually due to traces of copper. Ref. ind. 1.460 to 1.471. | Cineole, about 50 %; terpineol; terpenyl acetate; pinene, valeraldehyde (?); benzaldehyde (?). |

TABLE OF ESSENTIAL OILS—Continued

| Oil | Chief sources | Sp. gr. at 15° | Opt. rot.,° | Other characters | Known constituents |
|---|---|---|---|---|---|
| Calamus......... | Fresh herb of *Acorus calamus* (S w e e t Flag). | 0.964 | +20.7 | Closely resembles the oil from the rhizome. | Acetic, œnanthilic, heptylic, and palmitic acids; eugenol; asarylic aldehyde; asarone; calameone; parasarone; and a bluish fraction. |
| | Rhizome. | 0.958–0.970 | +9 to +35 | Thick brownish liquid with a bitter taste. Ref. ind. 1.507 to 1.515. | |
| | Japanese. | 0.970 to 0.995 | .............. | Much more soluble in dilute alcohol than the German variety. | |
| Camphor......... | By-product in preparation of common camphor by the distillation of wood of *Cinnamomum camphora*. | 0.870–1.040 | +12 to +32 | Very variable in character. Fractional distillation affords commercial light camphor oil (sp. gr. 0.870) and heavy oil (1.000). | "See text." |
| | Leaves of camphor tree. | 0.932 | +4.9 | Liquid portions (separated from camphor) have properties of above camphor oils. | Large amount of camphor. |
| Camphor-wood (Venezuelan). | From Venezuelan wood of unknown origin. | 1.155 | +2.7 | Solidifies to a crystalline mass (apiole) at ordinary temperatures. | Apiole (parsley-apiole), 90%. |
| Cananga......... | (See *Ylang-Ylang Oil.*) | | | | |
| Canella.......... | Bark of *Canella alba.* | 0.920 to 0.935 | +1 to +3 | Spicy odour and taste...... | Pinene; caryophyllene; cineole; eugenol. |
| Caparrapi....... | Wood of *Nectandra caparrapi.* | 0.915–0.935 | −3 | Pale yellow to brownish-red oil. Acid reaction to litmus. Odour sweet and resembling chloral. | Caparrapic acid (monobasic), melting at 84.5°, a sesquiterpene alcohol (caparrapiol). |

| | Source | Sp. gr. | Rotation | Properties | Constituents |
|---|---|---|---|---|---|
| Caraway.......... | Fruit of *Carum carvi.* | | .......... | .......... | Dextro-limonene; carvone; di-hydrocarvone, carveol, dihydrocarveol. |
| | S. & Co. | 0.908–0.918 | +70 to +85 | Characteristic odour and spicy taste. Distils mainly above 200°, not more than 15 % should distil below 185°. Ref. index 1.484 to 1.4897. | |
| | Brit. Pharm. | 0.910–0.920 | .......... | | |
| Cardamoms....... | Seed of *Elettaria cardamomum.* | | | | Terpinene; dipentene; limonene; terpineol: acetic esters. Terpineol acetate, cineole. |
| | (Ceylon.) S. & Co. | 0.923–0.946 | +24 to +47 | Ref. ind. 1.460–1.470 | |
| | B. & Co. (Bengal.) S. & Co. | 0.895–0.906 0.930–0.940 0.920 | +12 to +15 +30 −12.7 | Camphoraceous odour and taste. Ref. ind. 1.4639. Distils chiefly below 220°. Ref. ind. 1.465. | Large amount of cineole. (See Text.) |
| Carrot (wild)..... | Fruit of *Daucus carota.* | 0.870–0.945 | −11 to −37 | Sharp taste.......... | Pinene; limonene daucol, butyric and palmitic acids. |
| Cascarilla......... | Bark of *Croton Eluteria* and *C.cascarilla.* | 0.898–0.928 | +1 to +14 | Ref. ind. 1.49100 to 1.496. | Terpenes; palmitic and stearic acids (traces); cascarillic acid (2 %); traces of eugenol and cymene and oxygenated bodies. |
| Cassia............ | Bark of *Cinnamomum cassia.* | 1.055–1.072 | +6 to −1 | Ref. ind. 1.602 to 1.606 | Cinnamic aldehyde, 70–85 %; cinnamic esters, o-methyl-coumaric aldehyde. |
| Cedar-leaf (American). | Leaves of red cedar, *Juniperus Virginiana.* S. & Co. | 0.887–0.900 | +55 to +65 | .......... | Limonene; cadinene; borneol; bornyl esters. |
| | | 0.887 | +59.4 | Pale greenish-yellow. Medicinal properties probably similar to the official oil of savin. | |
| Cedar-wood (American) | Wood of *J. Virginiana.* | 0.940–0.960 | −25 to −4 = −47 | Ref. ind. 1.498 to 1.505. | Cedrol cedar-camphor. Cedrene, cedrenol, pseudo-cedrol. |
| Cedrat............ | (See *Citron Oil.*) | | | | |

## TABLE OF ESSENTIAL OILS—CONTINUED

| Oil | Chief sources | Sp. gr. at 15° | Opt. rot.,° | Other characters | Known constituents |
|---|---|---|---|---|---|
| Cedrela wood...... | Wood of *Cedrela odorata.* | 0.923 to 0.950 | Variable | Light blue to yellow........ Ref. ind. 1.504. | Probably cadinene. |
| Celery........... | Fruit of *Apium graveolens.* | 0.870 to 0.895 | +60 to +82 | Ref. ind. 1.478 to 1.486. | Dextro-limonene, but no pinene (distinction from oil of turpentine); a very small quantity of palmitic acid and phenols; sedanolide, sedanonic acid, sedanolic acid, selinene. |
|  | *S. & Co.* *B. & Co.* | 0.880–0.890 0.8730; 0.8777 | +67 +75; +71.6 |  |  |
|  | Green herb of *A. graveolens.* | 0.848–0.880 | +41 to +60 | Ref. ind. 1.478 to 1.481... | .................. |
| Chamomile, German. | Flower-heads of *Matricaria Chamomilla.* | 0.920–0.955 | Very slight. | Bluish colour, changing to green and brown on exposure to light. Bitter taste. | Solidifies to a buttery mass at a low temperature, owing to the presence of a paraffin, melting at 53°–54°. The oil appears to contain esters. |
| Roman. | Flower-head of *Anthemis nobilis.* | 0.904–0.918 | −3 to +4 | Bluish colour when fresh, changing in the light to greenish or brownish-yellow. Burning taste. Ref. ind. 1.4455. | Isobutyl isobutyrate and angelate; amyl and hexyl tiglates and angelates; anthemol. The ester content appears to be much less than that of English oils (containing 80% esters). |
| Champeca. (See *Guaiacumwood, Oil.*) | Flowers of *Michelia Champaca........* Java. Manila. | 0.954 to 1.02(30°) 0.904–0.9107(30°) |  | Ref. ind. 1.455–1.483(30°) Ref. ind. 1 464–1.468 | Benzoic acid. Benzyl alcohol, linalol, geraniol esters of methyl ethyl acetic acid, methyl anthranilate, iso-eugenol, methyl eugenol. |
|  | Flowers of *Michelia longifolia,* Java. | 0.883 to 0.897 | −12.8 | Ref. ind. 1.447 (30°). Very volatile, odour resembling basilicum...... | .................. |

| | | | +23.5 | Yellow-green colour, pleasant odour. | Pinene; cineole. |
|---|---|---|---|---|---|
| Cheken-leaf...... | Leaves of *Myrtus, cheken.* | 0.880 | | | |
| Chenopodium (American wormseed). | Fruit of *Chenopodium anthelminticum ambrosioides.* Commercial Oils. | 0.955–0.990 | −4 to −10° | Penetrating odour and bitterish taste. Varies in character according to age. | Ascaridole, cymene, α-terpinene, an opt. act. terpene not identified. |
| | Leaves of *C. ambrosioides.* | 0.879 | −33 | Odour of trimethylamine. | .................. |
| Chione Glabra... | Bark of *Chione glabra* (West Indies). | ............. | ............. | Curious and objectionable odour. | Ortho-hydroxy-acetophenone. |
| Cinnamon, Ceylon. | Bark of *Cinnamomum zeylanicum.* | 1.023 to 1.040 | 0 to −1 | Sol. in 3 vols. 70% alcohol. Ref. ind. 1.58 to 1.59. | Cinnamic aldehyde, phellandrene, eugenol. (See Text.) |
| Cinnamon, Japanese...... | (See *Nikkei Oil.*) | ............. | ............. | .................. | Limonene, citral, dipentene. |
| Cinnamon leaf.... | From *C. zeylanicum*... | 1.045 to 1.065 | −1 to +3.4 | Ref. ind. 1.5310 to 1.540 | Eugenol, cinnamic aldehyde, safrol, linalol, benzaldehyde. |
| Citron........ | Fresh peel of *Citrus medica.* | 0.851 to 0.854 | +77 to +82 | Ref. ind., 1.475 at 20°. Contains minute white crystals. | A crystalline substance containing $C_{18}H_{18}O_4$. M.p. 145°. |
| Citronella...... (See Text). | Grass of *Cymbopogon (Andropogon) nardus* | 0.885–0.920 | ............. | Ref. ind. 1.480 to 1.483 Java and Singapore oil 1.465 to 1.468. | Citronellal, geraniol, borneol, linalol, camphene, dipentene, limonene, methyl heptenone. |
| Cintronella (Java Verbena). | Fruit of *Tetranthera polyantha var. citrata.* | 0.895–0.898 | +6 to +13 | Verbena-like odour, and has therefore been called "Oil of Verbena, Java." | Citral; geraniol, geranyl esters. |
| | Leaves of above. | 0.896–0.917 | −12 to −16 | Ref. ind. 1.4644. | Cineole, citral, geraniol (?). |
| | Bark of above. | 0.866–0.906 | +10 to +21 | .................. | Citral, citronellal, 56.5% alcohols (geraniol?). |

## TABLE OF ESSENTIAL OILS—Continued

| Oil | Chief sources | Sp. gr. at 15° | Opt. rot., ° | Other characters | Known constituents |
|---|---|---|---|---|---|
| Clove......... | Flower-buds of Eugenia caryophyllata. | 1.043–1.068 | Slightly lævorotatory (0° to 1° 30'). | ............ B. p. 250–260°, greater part distilling between 250–251°. Becomes darker and thicker with age. Spicy taste. Ref. ind. 1.530 to 1.535. | ............ Methyl alcohol; furfural; 90% of eugenol; caryophyllene, two modifications; acet-eugenol. Methyl-n-amylketone. Methyl-n-amyl carbinol. Methyl alcohol; furfurol; eugenol; caryophyllene, two modifications. |
|  | Flower stems........ | 1.040–1.067 | To −1.5 | Odour not so fine as true oil of clove. |  |
| Clove leaves...... | Leaves of E. caryophyllata. | 1.032 to 1.065 | −0.8 to −1.85 | Ref. ind. 1.5333 to 1.5391. | Eugenol. |
| Cochlearia (synthetic). | ............ | 0.944 (at 12°) | ............ | B. p. 159–160°. In commerce a mixture consisting of oil of mustard and oil of rue is frequently sold as oil of cochlearia, but has not the properties of true oil. | Secondary butyl thiocarbimide. |
| Cognac...... | ............ | 0.872–0.890 | −0.05 to +0.75 | Acid number 29 to 100: ester number 140 to 250 sol. in 2 parts of 80% alcohol. Ref. ind. 1.427 to 1.432. | Caprinic acid, caprylic acid, with esters. |
| Conium...... | Fruit of Conium maculatum. Herb of C. maculatum. | 0.831 0.931 at 20° | −2.2 −12.4 | ............ ............ | ............ Palmitic acid. |
| Copaiba......... | Oleo-resin of Copaifera Landsorfii, and other species. S. & Co. | 0.890–0.910 0.886–0.910 | Lævorotatory to −5 to −35 −2.5 to −33 | Bitterish and pungent taste. Has same effects upon the system as copaiba. ............ | Chiefly caryophyllene. ............ |

| | | | | | |
|---|---|---|---|---|---|
| Coriander......... | Fruit of *Coriandrum sativum*. | 0.863–0.885 | +7 to +14 | Warm, spicy taste. Ref. ind. 1.4635 to 1.4760. | Dextro-linalol, pinene. |
| Costus........... | Root of *Aplotaxis lappa*. | 0.940–1.009 | +13 to +26 | About half distils over below 315°. Ref. ind. 1.5216. | Camphene, phellandrene, costene, aplotaxene, costol, costus-lactone, costus acid. |
| Cubebs........... | Unripe fruit of *Piper cubeba*. | 0.905 to 0.930 | −25 to −40 | Pale greenish or yellowish oil, with a warm camphoraceous, aromatic taste. When old, or distilled from old fruit, also contains cubeb camphor. Ref. ind. 1.493 to 1.497. | Chiefly cadinene, with some dipentene. |
| Culilaban......... | Fruit of *Cinnamomum Culilavan*. | 1.051 to 1.055 | ............... | Odour of eugenol; dark in colour. | Eugenol, methyl-eugenol; terpineol |
| Cumin............ | Fruit of *Cuminum cyminum*. | 0.893–0.930 | +3 to +8 | Limpid liquid with a sharp spicy taste. Ref. ind. 1.494 to 1.507. | Cuminaldehyde, cuminic alcohol, dipineol, terpineol, dipentene, cymene, pinene. |
| Cypress.......... | Leaves of *Cypressus sempervirens*. French / German | 0.868–0.884 / 0.880–0.900 | +12 to +31 / +4 to +13 | Ref. ind. 1.471 to 1.4760. Ref. ind. 1.474 to 1.480. Sol. 3 to 7 of 90% alcohol. | d-Pinene; l-cadinene; furfurol; d-camphene; d-sylvestrene; cymene; a ketone; sabinol; acetate of d-terpineol (m. p. 35°); valeric acid; cedrol. |
| Damiana.......... | *Turnera diffusa* and other species. | 0.940–0.970 | −23.5 | Greenish viscid liquid, with an odour of chamomile. B. p. 250° and 310°. | A blue oil in the higher fractions; a paraffin. |
| Dill.............. | Fruit of *Anethum graveolens*. | 0.900–0.918 | +70 to +82 | Penetrating odour, and sweetish, afterward sharp and burning taste. Odour quite different from East Indian dill oil. Ref. ind. 1.480 to 1.495. | Limonene; carvone; a paraffin. phellandrene, dill-apiole. |
| East Indian. | *Anethum sowa*......... | 0.948 to 0.970 | +41.5 to +47.5 | ............... | Limonene; dill-apiole; carvone. |
| Dog-fennel........ | Entire plant of *Esparatorium fœniculaceum*. | 0.926–0.935 | +17.9 to +18.5 | ............... | Phellandrene. |

TABLE OF ESSENTIAL OILS—Continued

| Oil | Chief sources | Sp. gr. at 15° | Opt. rot., ° | Other characters | Known constituents |
|---|---|---|---|---|---|
| Elder otto | Elder blossom (Sambucus nigra). B. & Co. | 0.8461 (at 30°) 0.8277 (at 30°) | .......... | M. p., 28.2°; saponification value 75.4; after acetylation, 97.9. M. p., 28°. | .......... |
| Elemi | Oleo-resin of Manila Elemi canarium luzonicum. | 0.870–0.915 | +30 to +55 | Agreeable aromatic odour and taste. Ref. ind. 1.4775–1.490. | Phellandrene; dipentene; limonene; allyltrimethoxy—3, 4, 5—benzene; elemol. |
| Elecampane | Root of Inula helenium. | 1.013 to 1.038(30°) | +120 to +123.75 | Ref. ind. 1.522. | Alantic acid; alanto-lactone; alantol; iso-alantolactone. |
| Erigeron (or flea-bane.) | Fresh flowering herb of Erigeron Canadensis. | 0.855–0.870 (increasing with age). | +52 + 83 | Peculiar persistent odour and slightly pungent taste. Larger part distils between 175° and 180°. | Limonene; terpineol, and esters. Trace of citronellal. |
| Eriodictyon | Leaves of E. Californica. | 0.937 | −1.6 | Sol. in 70% alcohol. | .......... |
| Estragon (Tarragon). | Herb of Artemisia Dracunculus. | 0.900–0.946 | +2 to +10 | Peculiar anise-like odour. Ref. ind. 1.5028–1.5134. | Methyl-chavicol. Phellandrene. |
| Eucalyptus | (See page 52.) | .......... | .......... | .......... | .......... |
| Fennel | Fruit of Foeniculum vulgare and other species. | 0.960–0.980 | +12 to +24, + 6 to +20 | Between 5° and 10° usually solidifies to a crystalline mass. Ref. ind. 1.525 to 1.538. | Pinene; phellandrene; dipentene; limonene; fenchone; anethol (usually about 60%). Oils from different sources never contain all these constituents simultaneously. |
| Feverfew | (See Pyrethrum Oil.) | 0.900 to 0.960 | .......... | .......... | Borneol and esters. |
| Fir-cone | Cones of Abies alba. | 0.851–0.875 | −60 to −84 | .......... | Pinene, limonene, bornyl acetate. |
| Fleabane | (See Oil of Erigeron.) | 0.855–0.870 | +52 +83 | .......... | .......... |

| | | 0.870 | +8 | Light brown oil; sol. in 90% alcohol. | |
|---|---|---|---|---|---|
| Fœnugreek...... | Seeds of Trigonella fœnumgræcum. | | | .......... | .......... |
| Frankincense..... | (See Oil of Olibanum.) | .......... | .......... | .......... | .......... |
| Galangal......... | Rhizome of Alpinia officinarum. | 0.915–0.925 | –1 to –6 | B. p. 170°–275°; sol. in ½ part of 90% alcohol. Ref. ind. 1.476 to 1.4825. | Cineole; eugenol. pinene, cadinene. |
| Galbanum......... | Gum-resin of Ferula galbaniflua. | 0.905–0.955 | –10 to +20 | Yellowish oil of aromatic odour. Ref. ind. 1.484 to 1.4863. | d-pinene; cadinene; cadinol |
| Gardenia......... | Fresh flowers........ | 1.009 | +3.0 | B. p. 204° with partial decomposition. | Benzyl acetate; styrolyl acetate; linalol; linalyl acetate; terpineol; methyl anthranilate. |
| Garlic........... | Allium sativum........ | 1.045–1.060 | Inactive. | .......... | Allyl-propyl-disulphide; diallyl-disulphide. |
| Geranium (rose geranium). | Herb of several species of Pelargonium, especially P. Radula, P. capitatum and P. odoratissimum. | | | Pale yellowish or greenish (réunion) oil, having an agreeable rose-like odour. Ref. ind. 1.460 to 1.471. | Geraniol and citronellol (free, and combined as tiglates). Total alcohols 60 to 75% (of which 15 to 25% exist as esters). |
| | Algerian. | 0.802–0.904 | –6 to –12 | | |
| | French. | 0.804–0.905 | –7 to –12 | | |
| | Réunion. | 0.886–0.895 | –8 to –14 | | |
| | Spanish. | 0.898–0.907 | About –8 to –11 | | |
| Geranium, East Indian (so-called Turkish geranium or Palmarosa oil). | From grass of Cymbopogon martini. | 0.885–0.900 | –3 to +6 | Ref. ind. 1.472–1.478. | Geraniol; geranyl acetate and capronate; dipentene; methyl heptenone (?) farnesol. Total alcohols 75 to 95% (of which less than 10% exist as esters), consisting chiefly of geraniol, with very little or no citronellol. |

## TABLE OF ESSENTIAL OILS—Continued

| Oil | Chief sources | Sp. gr. at 15° | Opt. rot.,° | Other characters | Known constituents |
|---|---|---|---|---|---|
| Ginger......... | Rhizome of *Zingiber officinale*. | 0.875–0.886 | −28 to −50 | Aromatic, somewhat burning taste. Ref. ind. 1.4795 to 1.4855. | Camphene; phellandrene; *l*-zingiberene, ineole, citral, borneol, decylaldehyde, methylheptenone, nonaldehyde, linalol, chavicol, zingiberol. |
| Ginger-grass oil... | ................. | 0.900 to 0.955 | −30 to +50 | Ref. ind. 1.47850–1.495. | Geraniol, dipentene, phellandrene; limonene; perillic alcohol. |
| Golden rod (Canadian). | Flowering herb of *Solidago Canadensis*, etc. | 0.859 | −11.2 | ................. | Contains 85% of terpenes, mainly pinene with a little phellandrene and dipentene; possibly limonene; borneol; bornyl acetate; cadinene. |
| Grains of Paradise | Seeds of *Amomum melegueta*. | 0.894 | −4 | Distils mainly at 257°–258°. Ref. ind. 1.4912. | Cineole, bisabolene. |
| Grape-fruit (shaddock). | Fruit of *Citrus decumana*. | 0.845; 0.870 | +72.5 to +94.5 | Odour of bitter orange oil. Ref. ind. 1.475–1.4785. | Pinene, limonene, linalol, citral, geraniol. |
| Guaiacum wood ("b a l s a m wood"). | Wood of guaiacum species, probably *Bulnesia sarmienti*. | 0.965–0.975 at 30° | −3 to −8 | Very viscid oil. Violet and tea-like odour, and crystalline at ordinary temperatures. Ref. ind. 1.503–1.505. | Crystallisable guaiol, m. p. 91°. A sample of so-called "Champaca-wood oil" was found by S. & Co. to be Guaiacum-wood oil. |
| Gurjun balsam... | Balsam of *Dipterocarpus* species. | 0.918–0.930 | −35 to −130 | Ref. ind. 1.503–1.505. | A sesquiterpene; small amounts of alcohols. |
| Hedeoma, American. | Dried leaves and tops of *Hedeoma pulegioides*. | 0.925–0.960 | +17 to +23 | Limpid liquid with a mint-like odour and taste. Forms a clear solution with 2 volumes or more of alcohol (70%). Ref. ind. 1.4800. | Pulegone, menthone, 1 methyl, 3 cyclo hexanone, l-pinene, *l*-limonene, dipeptene. |

| | | | +15 to +25 | Ref. ind. 1.4815 to 1.4865. | Pulegone, limonene, dipentene, menthol, menthone. |
|---|---|---|---|---|---|
| Hedeoma (Penny-royal). | Leaves of Mentha pulegium. | 0.930–0.960 | | | |
| Hedychium........ | Flowers of Hedychium coronarium. | 0.869 | −0.5 | ............... | ............... |
| Helichrysum..... | Flowering herb of Helichrysum augustifolium. | 0.892–0.920 | +4 to −10 | Ref. ind. 1.4745–1.4849. | Nerol. |
| Hemp.......... Indian. | Dried herb of Cannabis sativa. Herb of C. indica.... | 0.932 · 0.930 | −10 to −12 · −10 | ............... | Terpenes; sesquiterpenes, cannibene. Cannibinol. |
| Heracleum...... | Fruit of Heracleum spondylium. | 0.865–0.880 | 0 to +2 | Ref. ind. 1.426–1.433. | Ethyl butyrate; hexyl and octyl acetates; octyl capronate. |
| Hop.......... | Flowers of Humulus lupulus. | 0.850–0.893 | −2 to +2 | Ref. ind. 1.4855–1.492. | Dipentene, caryophyllene, linalol, myrcene, and several acids. |
| Horsemint (see Monarda Oil). | Herb of Monarda punctata. | 0.930–0.940 | Slightly + | Yellowish-red or brownish-red colour and a strong thyme-like odour. | Thymol; carvacrol; cymene, limonene. |
| Hyssop.......... | Herb of Hyssopus officinalis. | 0.925–0.940 | −17 to −24 | Ref. ind. 1.473–1.486. | Possibly thujone or thujyl alcohol. β-Pinene; l-pinocamphone. |
| Iva.......... | Dried flowering herb of Achillea moschata. | 0.928 to 0.960 | −12 to −15 | Light blue colour. Ref. ind. 1.4761. | Cineole; l-camphor; palmitic acid. |
| Jasmine........ | Flowers of Jasminum grandiflorum. | 0.920–1.015 | −1 to +4 | ............... | Benzyl acetate; linalyl acetate; benzyl alcohol; linalol; indole; methyl anthranilate; jasmone. p-cresol; geraniol. |
| Juniper.......... | Fruit of Juniperus communis. Brit. Pharm. S. & Co. | 0.867–0.875 · 0.865–0.890 · 0.865–0.885 | −3 to −15 · Inactive or to −18 | Becomes dark and thicker by exposure to air. Has a somewhat terbinthinate and bitter taste. Ref. ind. 1.474 to 1.488. | Chiefly pinene with some cadinene; juniper-camphor. Camphene, terpinenol. |

TABLE OF ESSENTIAL OILS—Continued

| Oil | Chief sources | Sp. gr. at 15° | Opt. rot.,° | Other characters | Known constituents |
|---|---|---|---|---|---|
| Kämpferia........ | Rhizome of Kaempferia rotunda. | 0.890 to 0.900 | +12 | Odour at first of camphor, then reminding of estragon oil. | Cineole. Odour suggests probable presence of methyl-chavicol. |
| Kiku............. | Leaves of Pyrethrum indicum. | 0.880–0.932 | ............ | Ind. ref. 1.4931. | ............ |
| Kobushi......... | Fresh leaves and twigs of Magnolia kobus. | 0.9432 to 0.9642 | -1.1 to -1.5 | Sassafras-like odour....... | Safrol, citral, cineole, anethol, methyl-chavicol. |
| Kuro-moji (Japan) | Wood of Lindera sericea. | 0.890-0.915 | -0.1 | Balsamic odour......... | Dextro-limonene; dipentene; terpineol; levocarvone. |
| Lantana......... | Herb of Lantana camara (Philippine). | 0.9132(30°) | +11.5 | 1.4913(30°) | ............ |
| Laurel.......... | Leaves of Laurus nobilis. | 0.915-0.932 | -15 to -22 | ............ | Pinene, cineole, geraniol, eugenol, linalol. |
| California. | Leaves of Umbellularia Californica. | 0.935-0.950 | -22 to -24 | Agreeable but afterward irritating odour. Sol. in 1.5 parts 70% alcohol. | Umbellulone, cineole, eugenol, methyl-eugenol, l-pinene, safrol, fatty acids (traces). |
| Lavender......... | Fresh flowers of Lavandula vera.<br>French flowers. | ............ | ............ | ............ | ............ |
|  |  | 0.883-0.900 | -3 to -10 | Ref. ind. 1.460 to 1.4660. | Linalol; linalyl acetate (30 to 45%); geraniol; carophyllene, small amounts of limonene, pinene and cineole, nerol, coumarin, borneol, furfural, ethyl-amyl-ketone. |
|  | English Flowers. | 0.883-0.900 | -3 to -10 | The content of esters in the French oil is usually about 3 times as high as English oil. | Much cineole; limonene; linalyl acetate (7 to 10%). Chiefly linalyl acetate (10.7% esters), and as above. |

| Oil | Botanical source | Specific gravity | Rotation | Properties | Constituents |
|---|---|---|---|---|---|
| Lavender...... | Spanish flowers...... (Bot. source unknown.) | 0.900; 0.914 | −5 to +4 | Ref. ind. 1.464 to 1.466. | These oils contained 1.8% and 7.7% of esters (as linalyl acetate), and 44.5 and 50.5% free alcohol (as linalol). |
| Portuguese. | Flowers of *L. pedunculata.* | 0.939 | −44.9 | Indistinct and not very pleasant odour. | Linalyl acetate 39%; thujone; cineole. |
| | Flowers of *L. dentata.* | 0.942–0.963 | +32 to +44 | Distils almost completely between 170–200°. Has an odour resembling rosemary and camphor. | *d*-camphor; *d*-fenchone. |
| | Flowers of *Lavandula stoechas.* | 0.930–0.935 | −36 to −40 | Distils between 180–245°. Has an odour resembling rosemary and camphor. | Cineole; pino-camphor. |
| Lavender, spike... | Flowering herb of *Lavandula spica.* | 0.905–0.920 | −3 to +7 Rarely over +5 | Much less fragrant than the official oil. Has odour reminding both of rosemary and lavender. Ref. ind. 1.4640–1.468. | Pinene, camphene, cineole, linalol, camphor, borneol, terpineol, geraniol, practically no esters. |
| Ledum.......... | (See *Marsh-tea Oil.*) | .......... | .......... | .......... | .......... |
| Lemon.......... | Fresh lemon-peel of *Citrus medica,* var. *limonum.* | 0.856–0.862 | +57 to +61 | Bitterish taste. Ref. ind. 1.475 to 1.4775. | Limonene; citral; citronellal; linalylacetate; camphene; phellandrene; methyl heptenone; γ-terpinene; α-terpineol; bisabolene; cadinene; citroptene, and according to Umney and Swinton, geranyl acetate; possibly also other esters of geraniol and citronellol. |
| Lemon-grass (verbena; Indian Melissa). | Grass of *Cymbopogon (Andropogon) citratus.* | 0.895–0.905 | +1 to −5 | Fragrant odour, reminding of lemon and verbena. Ref. ind. 1.483 to 1.4885. | Citral; geraniol; methylheptenone; citronellal; decylic-aldehyde, linalol, dipentene, limonene. |
| Lemon thyme..... | *Thymus hyemalis.*..... | 0.901 to 0.908 | +9.7 to 18.5 | .......... | .......... |

## TABLE OF ESSENTIAL OILS—CONTINUED

| Oil | Chief sources | Sp. gr. at 15° | Opt. rot., ° | Other characters | Known constituents |
|---|---|---|---|---|---|
| Lime, Italian...... | Rind of fresh fruit of *Citrus limetta* (by expression). | 0.870–0.875 | +34 to +40 | Golden-yellow oil, with refreshing odour. Ref. ind. 1.4782–1.4851. | Limonene, citral, linalol, linalyl acetate (26%). |
| | Distilled oils. | 0.8450–0.8858 | +33 to +35 | .................... | Citral (6.3 to 8%), and bisabolene. |
| Lime-flowers...... | Flowers of *Citrus limetta*. | 0.870 | +21.5 | .................... | Linalol, methyl anthranilate. |
| Lime, West Indian (Limette). | Rind of fresh fruit of *Citrus medica*, var. *acida* (by expression). | 0.878–0.901 | +32 to +38 | Lemon odour. 18% of non-volatile residue. Ref. ind. 1.482 to 1.486. | A paraffin, citral, limonene; methyl anthranilate; citroptene, bisabolene, *l-α*-terpineol. |
| | Distilled oil. | 0.856–0.870 | +33 to +47 | Unpleasant odour. 3% non-vol. residue. Ref. ind. 1.4702 to 1.4707. | |
| Linaloe (Ligmaloe). | Mexican wood of *Bursera* species. | 0.870–0.898 | −3 to −15 | Ref. ind. 1.460 to 1.465. | Chiefly linalol; terpineol, methyl-heptenone, geraniol, myrcene, methyl-heptenol. |
| | Guiana wood (*Bois de rose femelle*). | 0.870–0.880 | −10 to −20 | Fragrant oil. Resembles the Mexican wood oil. Ref. ind. 1.461 to 1.4635. | Linalol (almost wholly), nerol, dipentene. |
| Lovage........... | Dried root of *Levisticum officinale*. | 1.00–1.049 | 0 to +7 | Sol. in 2 to 4 parts of 80% alcohol. Ind. ref. 1.539 to 1.552. | *d*-terpineol; a terpene. |
| Mace........... | Arillode of seed of *Myristica fragrans*. | 0.890–0.932 | +10 to 22 | Agreeable odour. Ref. ind. 1.476 to 1.484. | Pinene, dipentene, myristicin. (See nutmeg). |
| Mandarin........ | (See *Orange Oil, Mandarin*.) | .................... | .................... | .................... | .................... |
| Marjoram........ | Fresh herb of *Origanum Marjorana*. | 0.895–0.910 | +15 to +20 | Ref. ind. 1.472 to 1.476. | Terpinene, *d-α*-terpineol, terpinenol-4. |

| | | Specific gravity | Optical rotation | Properties | Chief constituent said to be |
|---|---|---|---|---|---|
| Marsh Tea (Ledum). | Herb of *Ledum palustre*. Leaves......... Flowering twigs... | 0.925 to 0.963 | −4.33° | Pale reddish-yellow colour and penetrating odour. Boils between 180°–250° when free of ledum camphor. | Ledum-camphor. |
| Masterwort......... | Root of *Imperatoria ostruthium*. | 0.862 to 0.877 | +59 to +66 | ............ | Dipentene, limonene, pinene, phellandrene, esters. |
| Massoy Bark...... | Bark of *Massoia aromatica*. | 1.04–1.065 | +1.75° | Agreeable spicy odour reminding of clove and nutmeg, and a sharp burning taste. | Eugenol (75%), safrole, pinene, limonene, dipentene. |
| Maté......... | Dried leaves of *Ilex Paraguayensis*. | 0.8875 | +3.73 at 20° | Solid, melts at 26.5°. Sol. in absolute alcohol. | ............ |
| Matico......... | Leaves (and flowers) of *Piper angustifolium* and other sp. of piper. | 0.938 to 1.135 | −30° to +6° | Yellowish-brown colour and peculiar odour. Ref. ind. 1.496 to 1.5290. | Dill-apiole, small amount of parsley-apiole, a phenol, possibly methyl eugenol, asarone. |
| Meadowsweet...... | Herb of *Spiræa ulmaria*. | ............ | ............ | ............ | Methyl salicylate. |
| Melaleuca (see text). | Leaves of sp. of *Melaleuca*. | 0.919 to 0.930 | 0 to −4 | Ref. ind., 1.465 to 1.471. | Cineole, terpineol; terpinyl acetate; *l*-α-pinene. |
| Melissa......... | Herb of *Melissa officinalis*. | 0.895–0.925 | 0 to −0.5 | Ref. ind. 1.474 to 1.484. | Citral, citronellal, geraniol, linalol, citronellol. |
| Mew......... | Dried root of *Meum athamanticum*. | 1.001 | ............ | Above 300° gives greenish-blue fractions. | ............ |
| Michelia......... | (See *Champaca Oil*.) | ............ | ............ | ............ | ............ |
| Monarda (see Horsemint Oil). | Herb of *Monarda punctata* (Horse-mint). | 0.930–0.940 | Slightly + | Thymol separates on standing. | Thymol 60%, cymene, traces *d*-limonene, linalol, carvacrol. |
| | *M. fistulosa* (wild bergamot). | 0.916–0.941 | Slightly − | ............ | Carvacrol 55%, thymoquinone, thymo-hydroquinone, cymene, limonene. |
| | *M. citriodora*...... | (at 20°) 0.9437–0.9603 | ............ | ............ | Carvacrol, thymo-hydroquinone, citral 1%, cymene, thymol. |

TABLE OF ESSENTIAL OILS—Continued

| Oil | Chief sources | Sp. gr. at 15° | Opt. rot.,° | Other characters | Known constituents |
|---|---|---|---|---|---|
| Mountain mint... | Herb of *Pycnanthemum incanum.* | 0.910–0.940 | +3 to +5 | .......... | Carvacrol, pulegone. |
| Mugwort......... | (See *Artemisia oil.*) | .......... | .......... | .......... | .......... |
| Muskroot........ | Rhizome of *Ferula sumbul.* | 0.932–0.964 | −6° | Sol. in equal vol. of 90% alcohol. | .......... |
| Mustard......... | Sp. of *Brassica.* | 1.014–1.030 | Slightly + | Ref. ind. 1.5267 to 1.528. | Allyl iso-thiocyanate, carbon disulphide. |
| Myrcia.......... | (See *Bay Oil.*) | .......... | .......... | .......... | .......... |
| Myrtle.......... | Leaves of *Myrtus communis.* | 0.880–0.925 | +8 to +27.5 | Ref. ind. 1.463 to 1.470. | Pinene, cineole, dipentene, borneol, iso-borneol, myrtenol; geraniol; nerol. |
| Neroli.......... | (See *Orange-flower Oil.*) | .......... | .......... | .......... | .......... |
| Nigella......... | Seeds of *Nigella sativa.* / Seeds of *Nigella damascena.* | 0.875 to 0.877 / 0.895 to 0.916 | +1.5 to +2.3° / −7.8 to +1 | Boils between 170° and 260°. Ref. ind. 1.4836 to 1.4844. Blue fluorescence......... Ref. ind. 1.5582. | Damascenine. |
| Nikkei.......... | Leaves and young twigs of *Cinnamomum loureirii.* Root Bark. | 0.9005 / 0.982 | −8.75 | Yellow oil of pleasant odour, recalling citral and cinnamon. .......... | Aldehydes, 27% chiefly citral; linalol (40%), cineole. Cinnamic aldehyde. |
| Nutmeg.......... | Fruit of *Myristica fragrans.* | 0.859 to 0.924 | +8 to +30 | Darkens and thickens on exposure to air. Spicy taste. Ref. ind. 1.478 to 1.4895. | Chiefly pinene; myristicin; (see text). |
| Olibanum........ | Gum-resin of *Boswellia carterii* and other species. | 0.875–0.894 | +15 to +30 | Balsamic odour faintly lemon like. Ref. ind. 1.4725–1.825. | Chiefly laevo-pinene; some phellandrene; dipentene: cadinene; and oxygenated substances. |

| | | | | | |
|---|---|---|---|---|---|
| Onion oil......... | Fresh herb and bulb of *Allium cepa*. | 1.035-1.045 | -3 to -6 | Dark brown oil......... | Allyl propyl disulphide. Allyl sulphide and terpenes are absent. |
| Orange flower (neroli oil). | Fresh flowers of *Citrus bigaradia* (Bitter Orange). | 0.870-0.885 | +1.5 to +5 | Fragrant odour and somewhat bitter taste. Ref. ind. 1.468 to 1.474. | Limonene; linalol; linalyl acetate; geraniol; nerol; a paraffin; methyl anthranilate; indol; d-terpineol; d-nerolidol; camphene; farnesol; esters. |
| | Fresh flowers of *Citrus aurantium* (Sweet Orange). | 0.860-08.933 | +16 to +30 | Ref. ind. 1.4728 to 1.4745.. | .................... |
| Orange peel (by expression). | Fresh peel of *Citrus bigaradia* (Bitter Orange). | 0.852-0.856 | +90 to +95 | Ref. ind. 1.472 to 1.4748. | Chiefly limonene; citral; d-linalol, nonylic and decylic alcohols; d-terpineol; decylaldehyde; esters; methyl anthranilate. |
| | *Citrus aurantium* (Sweet Orange). Expressed from unripe fruit. | 0.848-0.853 / 0.853 | +94 to +99 / +76.8 | Ref. ind. 1.472 to 1.475. | .................... |
| Orange, mandarin or tangerine. | Expressed from fresh peel of *Citrus nobilis*. | 0.854-0.860 | +65 to +75 | Ref. ind. 1.475 to 1.478. | Limonene; methyl ester of methyl anthranilate; dipentene. |
| Origanum......... | Herb of *Origanum hirtum*. | 0.940-0.980 | +1 to -1 | Golden-yellow colour when freshly rectified, reddish or reddish-brown on keeping. Penetrating aromatic, thyme-like odour. | Carvacrol (60 to 80%); cymene; terpenes. |
| | Herb of *Origanum smyrnæum*. | 0.895 to 0.966 | -1 to -15 | Ref. ind. 1.495 to 1.523. | Thymol; linalol; carvacrol (30-60%), cymene; pinene; d-camphor. |
| Orris root......... | Rhizomes of *Iris germanica, I. pallida,* and *I. florentina*. | .................... | Slightly+ | Melts at about 40° to 50°. Exquisite and persistent odour. | The original oil contains myristic acid (about 90%); oleic acid; methyl oleate and myristate; oleic aldehyde; irone, 10 to 15%. |
| Liquid oil......... | | 0.930 to 0.940 | +14 to +30 | Soluble in 80% alcohol, 1:8. Congeals at -5°. | |
| Palmarosa......... | (See *Geranium Oils*.) | | | | |

## TABLE OF ESSENTIAL OILS—CONTINUED

| Oil | Chief sources | Sp. gr. at 15° | Opt. rot., ° | Other characters | Known constituents |
|---|---|---|---|---|---|
| Paracoto.......... | Bark of a species of *Monimiaceae.* | 0.9275 | − 2.12 | Colourless oil of pleasant odour. | Cadinene; methyl-eugenol. |
| Parsley.......... | Fruit of *Petroselinum sativum,* S. & Co. | .............. | .............. | Ref. ind. 1.512 to 1.525. | ........................ |
| | Fruit of *Petroselinum sativum,* S. & Co. | 1.04–1.10 | − 4.5 to − 10° | Colourless or pale greenish yellow. | Pinene, apiole, myristicin, allyl-tetra-methoxy-benzene. |
| | Root of *P. sativum.* | 1.049 to 1.1012 | + 1.5 | Deposits crystals, probably apiol. | |
| | Herb of *P. sativum.* | 0.9023 to 1.016 | + 1° to 4° | Ref. ind. 1.509 to 1.525. | |
| Parsnip.......... | Fruit of *Pastinaca sativa.* | 0.870–0.890 | − 0.2 to − 0.5 | A yellow oil.............. | Ethyl alcohol, octyl butyrate, octyl propionate. |
| | | | | Ref. ind. 1.428 to 1.435. | |
| Patchouli.......... | Leaves of *Pogostemon patchouli.* | .............. | .............. | Yellowish-green or brown, somewhat thick oil, with a penetrating and persistent odour. Ref. ind. 1.507 to 1.513. | Cadinene (?), patchouli-camphor; a liquid sesquiterpene-alcohol; benzaldehyde, eugenol, cinnamic aldehyde, a ketone. |
| | Leaves of a species of *Pogostemon* (from Java). | 0.965–0.995 | − 50 to − 68 | | |
| | Leaves of a species of *Pogostemon* (from Java). | 0.925–0.940 | + 4 to − 34 | Occasionally deposits a stearoptene. | A substance having an odour resembling anise aldehyde. |
| | | | | Ref. ind. 1.50 to 1.506. | |
| Pennyroyal...... | (See *Oil of Hedeoma.*) | .............. | .............. | ........................ | ........................ |
| Pepper.......... | Fruit of *Piper nigrum.* | 0.870–0.915 | − 10 to + 14 | Ref. ind. 1.489 to 1.499. Strong pungent odour and taste. | Phellandrene, dipentene, caryophyllene. |
| | Fruit of *Piper longum* (Long pepper). | 0.861 | | Thickish oil of a light green colour, odour reminding of ginger. Boils at 250°–300°. | ........................ |
| Pepper, Japanese. | Fruit of *Xanthoxylum piperitum.* | 0.852 to 0.890 | − 26 to + 46 | Ref. ind. 1.4732 | Dipentene, *d*-limonene, cumic aldehyde, geraniol, phellandrene, palmitic acid. |

| | | | | | |
|---|---|---|---|---|---|
| Peppermint oils... | *Mentha piperita*...... | 0.896–0.930 | −18 to −33 | Ref. ind. 1.458 to 1.469. | Menthol, menthyl acetate (See text). |
| Persea............ | Dried leaves of *Persea gratissima*. | 0.955–0.960 | +1.9 to +25 | Greenish oil; ref. ind. at 18°. 1.51 to 1.515. | Methyl-chavicol; pinene; a paraffin. |
| Petit-grain........ | Leaves, twigs and occasionally unripe fruits of *Citrus bigaradia*. | 0.885–0.900 | +11 to −3 | Odour resembling neroli oil. ............ Ref. ind. 1.459 to 1.465. | Limonene, linalol, nerol, linalyl acetate, a sesquiterpene, camphene, β-pinene, dipentene, limonene, geraniol, methyl anthranilate. ............ |
| Petit-grain citronnier............ | Leaves and twigs of *Citrus medica*. | 0.868–0.894 | +14 to +35 | Contains oil from unripe fruit. | Camphene (?), limonene, linaloli (?). citral, geraniol. |
| Peucedanum....... | Fruit of *Peucedanum grande*. | 0.900 | +30 to +36 | B. p. 185–228°, leaving large residue. | ............ |
| Pichurim bean..... | Seeds of *Nectandra, pichury*. | 1.0306 at 17° | −49 at 16° | Fraction distilling between 255° and 256° is of a deep blue colour. Ref. ind. 1.5180. | Isoeugenol, safrol, cineole (?). |
| Pimento (allspice oil). | Nearly ripe fruit of *Pimenta officinalis*. | 1.025–1.055 | −1 to −5 | Becomes darker and thicker by age and exposure to the air. Clove-like odour and pungent spicy taste. Ref. ind. 1.525 to 1.534. | Closely resembles clove oil in composition and properties. Eugenol, caryophyllene, cineole, l-phellandrene, palmitic acid. |
| Pimpinella......... | Dried root of *Pimpinella saxifraga*. | 0.959 | ............ | Unpleasant odour resembling parsley. B. 240°. | ............ |
| Pine-needles...... | (See text)........ | ............ | ............ | ............ | ............ |
| Pittosporum ("m o c k - orange"). | Fruit of *Pimpinella undulatum*. | 0.8615 | +74 | ............ | d-α-pinene, limonene, a sesquiterpene, traces of esters. |

TABLE OF ESSENTIAL OILS—CONTINUED

| Oil | Chief sources | Sp. gr. at 15° | Opt. rot., ° | Other characters | Known constituents |
|---|---|---|---|---|---|
| Poplar.......... | Young buds of *Populus nigra.* | 0.890–0.905 | +2 to +6 | Odour of chamomile. Boils at 260°. | d-caryophyllene; a paraffin. |
| Pyrethrum (feverfew). | Flowering or dried herb of *Pyrethrum parthenium.* | 0.900–0.960 | .............. | Sap. value, 131.......... | Borneol and bornyl esters. |
| Ragweed.......... | Flowering herb of *Ambrosia artemissifolia.* | 0.870 | –26 | Deep green colour. | .............. |
| Rhodium.......... | (See *Rosewood Oil.*) | .............. | .............. | .............. | .............. |
| Rose.......... | Fresh flowers of *Rosa damascena* and other varieties. | 0.860–0.870 0.848–0.858(30°) | –1 to –4 | Fragrant odour, and mild, sweetish taste. Congealing-pt. about 16° to 30°. Ref. ind. 1.4580–1.4650. | Geraniol; citronellol; a paraffin esters; citral; linalol; nonyl aldehyde; phenylethyl alcohol; nerol; eugenol. |
| Rosemary.......... | Flowering tops of *Rosmarinus officinalis.* | 0.896–0.920 | –2 to +15 | Ref. ind. 1.465–1.4725. | Pinene; camphene; cineole; camphor; borneol and bornyl acetate. |
| Rosewood (rhodium). | Wood of *Convolvulus scoparius* and *C. floridus.* | 0.951 | +1.5 | Thick yellow oil of rose-like odour, crystallising in needles at about 12°. Commercial oil invariably mixture of rose and geranium oils, cedar wood and sandalwood. | Apparently chiefly a sesquiterpene. |
| Rue.......... | Herb of *Ruta graveolens.* (*Ruta bracteosa*). | 0.830–0.847 0.837 to 0.845 | 0 to +3 –1 to –5 | Greenish-yellow colour and characteristic odour. Solidifies at 5 to 11°. B. p. about 215–235°. Blue oil in high fractions (0.5%). Ketone solidifies at –10°. Both rue oils sol. in 2–3 vols. of alcohol (70%). | About 90% of methyl-nonyl-ketone; lauric aldehyde; small amounts of methyl-heptyl-ketone; methyl ester of methyl anthranilic acid. Methyl-heptyl-ketone; small amount of methyl-nonyl-ketone; an acetic ester; methyl-heptyl and methyl-nonyl carbinols; pinene; l-limonene; cineole; etc. |

| | | | | |
|---|---|---|---|---|
| Saffron. | Stigmas of Crocus sativus. | .... | .... | .... | Pinene; cineole; a paraffin; an oxygenated body; palmitic and stearic acids. |
| Sage (Dalmation). | Leaves of Salvia officinalis. | 0.915–0.930 | +2 to +25 | Penetrating characteristic odour. Ref. ind. 1.4575 to 1.468. | Thujone; borneol; pinene; cineole; salvene; d-camphor. |
| (Spanish) | Leaves of Salvia triloba(?). | 0.912–0.932 | +10 to +20 Rarely −. | .... | Similar to Dalmatian. |
| Sage (clary). (German) (French) | Leaves and flowers of Salvia sclarea. | 0.910–0.960 0.895–0.930 | −25 to −48° −10 to −63 | Odour of linalyl acetate Ref. ind. 1.477 to 1.504 Ref ind. 1.4040 to 1.4750 | Linalyl acetate; linalol. |
| Sandalwood. | Wood of Santalum album. | .... | .... | Yellowish thick oil, peculiar odour and pungent spicy taste. | Santal alcohols (94 to 98%); santalol, 3%: α, & β-santalenes; santalic acid; teresantalic acid; esters of santal alcohols. |
| Sandalwood. (East Indian) | .... | 0.973–0.981 | −13 to −21 | Saponification figure of the pure oil does not exceed 15. Ref. ind. 1.504 to 1.510. | .... |
| (West Indian) | Amyris balsamifera... | 0.955–0.965 | +19 to +30 | Ruby-red colour. | .... |
| (African) | Osyris tenuifolia(?)... | 0.948 to 0.963 | −42 to −61 | Sharp resinous empyreumatic odour. | Amyrol. |
| (W. Australian) | S. cygnorum... | 0.950 to 0.965 | Up to +5 | | Contains less santal alcohols than East Indian oils. |
| Sadalwood.—Continued. (S. Australian) | S. Preissianum... | 1.022 | .... | Cherry-red colour. Solidifies at about 6°. | A crystalline alcohol boiling at 101–103°. |
| Sassafras. | Leaves of Sassafras officinalis. | 0.872 | −6.5 | .... | Linalol; pinene; phellandrene; cadinene; a paraffin melting at 57°; geraniol; myrcene. |
| | Root-bark of S. officinalis. | 1.065–1.085 | +1 to +4 | Reddish-yellow oil with a warm taste. Ref. ind. 1.5275. | Safrol, 80%; camphor; pinene; phellandrene; eugenol; cadinene. |

## TABLE OF ESSENTIAL OILS—Continued

| Oil | Chief sources | Sp. gr. at 15° | Opt. rot., ° | Other characters | Known constituents |
|---|---|---|---|---|---|
| Saturcia... | Herb of *Satureja thymbra.* Fresh herb of *S. hortensis.* | 0.906 / 0.898–0.930 | ... / Up to −1 | Strong and penetrating thymol-like odour. / ... | Cymene; thymol, 19%; pinene; dipentene; bornyl acetate. Carvacrol (30%); cymene; pinene (?); traces of another phenol. |
| | Herb of *S. montana* (Mountain Savory). | 0.939 | +2.5 | Odour resembling common savory oil. | Carvacrol; and, according to Haller, another phenol and a terpene. |
| Savin... | Twigs of *Juniperus sabina.* | 0.907–0.930 | +38 to +62 | Ref. ind. 1.473 to 1.480. Becomes darker and thicker by age and exposure to air. Terebinthinate odour and pungent camphoraceous taste. | Pinene; cadinene; s a b i n o l, partly as acetate; sabinene; α-terpinene; citronellal; geraniol; dihydrocuminic alcohol; N-decyl aldehyde. |
| Savory... | (See *Satureja Oils.*) | ... | ... | | ... |
| Serpentaria... | Rhizome and roots of *Aristolochia serpentaria.* ("Virginian Snakeroot.") | 0.960–0.990 | +20 to +26 | Amber colour, and an odour resembling valerian and camphor. | Pinene; an ester of borneol; and a bluish-green fraction. |
| Shaddock... | (See *Grape-fruit Oil.*) | ... | ... | ... | ... |
| Snake-root... | (See *Asarum canadense. A. Europaeum,* and *serpentaria Oils.*) | ... | ... | ... | ... |
| Spearmint... | Fresh herb of *Mentha viridis.* | 0.920–0.940 | −30 to −50 | Becomes d a r k e r and thicker by age and exposure to air. Strong characteristic odour and warm taste. | Carvone; limonene; phellandrene; dihydrocarveol acetate. |
| Spike... | (See *Lavender Spike Oil.*) | ... | ... | ... | ... |

| | | | | Distils between 170°–300°. | Terpenes; methyl salicylate (10%). |
|---|---|---|---|---|---|
| Spicewood........ | Bark and twigs of *Laurus benzoin*. | 0.923 | ............ | ............ | ............ |
| Spoonwort........ | Fresh flowering plant of *Cochlearia officinalis*. | 0.933 to 0.960 | +52 to +70 | Distils between 150°–162°, leaving 5% of residue. Ref. ind. 1.4900. | Secondary butyl-iso-thiocyanate; benzyl-iso-thiocyanate. |
| Star anise........ | (See *Anise Oil, Star*.) | ............ | ............ | ............ | ............ |
| Sweet birch........ | Bark of *Betula lenta*... | 1.180–1.187 | Inactive. | B. p. 218–221°. Ref. ind. 1.5350. | Methyl salicylate, 99.8%; an ester, and a paraffin, etc. |
| Tansy............ | Herb of *Tanaceum vulgare* (American). | 0.925–0.935 | +24 to +34 | Ref. ind. 1.457–1.459. Becomes brown on exposure to light and air. Poisonous. | Thujone; camphor; borneol. |
| Tansy balsam...... | English Oil........ Herb of *Tanaceum balsamita*. | 0.943–0.949 | −25 to −35 −43.7 to −53.9 | Ref. ind. up to 1.4750. Balsamic odour, resembling common tansy. Distils between 207°–283°. | Much camphor. Contains a paraffin. |
| Tarragon......... | (See *Estragon Oil*.) | ............ | ............ | ............ | ............ |
| Tetranthera...... | Fruit of *Tetranthera citrata*. | 0.920 | ............ | ............ | ............ |
| Thuja............ | Leaves of *Thuja occidentalis* (so-called White Cedar). Commercial Oils. Root of *T. orientalis*. | 0.915–0.935 0.979 | −5 to −15 | Intense brown colour. | Thujone; *l*-fenchone: pinene; *l*-bornol. |
| Thyme........... | Leaves and flowering tops of *Thymus vulgaris*. | 0.900–0.950 | 0 to −4 | Yellowish-red oil, pungent, afterward cooling, taste. Ref. ind. 1.480 to 1.490 | Thymol, 20–30%; carvacrol; cymene; linalol; bornyl acetate; pinene; borneol. |
| Thyme, wild...... | Dried herb of *Thymus Serphyllum*. | 0.890–0.920 | −10 to −21 | Agreeable melissa-like aroma, with a slight odour of thyme. | Thymol; carvacrol; cymene. |
| | Herb of *T. camphoratus*. | 0.904 | ............ | ............ | Carvacrol (?); thymol (?); pinene; cymene; dipentene; bornylacetate. |
| | Herb of *T. capitatus*. | 0.901 | ............ | Strong thyme-like odour reminding somewhat of origanum. | Pinene; cymene; dipentene; bornyl acetate; thymol; carvacrol (?). |

TABLE OF ESSENTIAL OILS—Continued

| Oil | Chief sources | Sp. gr. at 15° | Opt. rot., ° | Other characters | Known constituents |
|---|---|---|---|---|---|
| Tuberose | Flowers | 1.007–1.043 | −2.5 to −3.75 | Odourous fraction distils at 80°–180° at 15 mm. pressure. | Methyl anthranilate; tuberone; benzyl benzoate; methyl benzoate; benzyl-alcohol. |
| Turmeric | Root of *Curcuma longa.* | 0.934 to 0.962 | −25° to +35° | Ref. ind. 1.5030 at 30°. | Phellandrene; turmerol; curcumone. |
| Valerian | Root of *Valeriana officinalis.* | 0.920–0.960 | −8 to −15 | Ref. ind. 1.4840–1.4868. Yellowish or brownish colour, characteristic, penetrating odour. | Pinene; camphene; limonene (?); borneol; bornyl formate, acetate and iso-valerate; terpineol (?); a sesquiterpene; an alcohol. |
| | Root of *Valeriana Cdtica.* | | | | |
| Japanese (Kesso oil). | Root of *V. officinalis*, var. *angustifolia.* | 0.960–1.004 | −20 to −35 | Ref. ind. 1.477–1.487. | Similar to European root oil but containing also kessyl acetate, and a blue fraction. Valeric acid (about 89%). |
| Mexican. | Root of *Valeriana Mexicana.* | 0.949 | Inactive. | | |
| Verbena | *Lippia citriodora* | 0.900–0.928 | −16 to +3 | | Citral; limonene; geraniol; verbenone; myrcene; cineol; methyl heptenone; citronellol. |
| Veti-ver | Grass, *Vetivera sisanoides.* | 1.015–1.040 | +25 to +37 | Ref. ind. 1.522–1.527. | Vetivenol; vetivene. |
| | Réunion oil | 0.982–1.020 | +10 to +38 | Most viscid of all essential oils. Ref. ind. 1.515–1.5285 | |
| Wartara | Seeds of *Xanthoxylum species.* | 0.8714 to 0.8740 | +5.5 to 6.5 | Coriander odour. | Linalol; dipentene; methyl cinnamate. |
| Wax-myrtle | Leaves of *Myrica cerifera.* | 0.9168 | −1.5 | Ref. ind. 1.4945 at 25° | |
| Wintergreen | Leaves of *Gaultheria procumbens.* | 1.180–1.187 | −0.45 to −1 | B. p. 218–221° | Methyl salicylate, 99%; an aldehyde. |

| | | | | Poisonous, Ref. ind. 1.465–1.469. | Cineole; dipentene; terpenine; α-terpineol; terpineol. |
|---|---|---|---|---|---|
| Wormseed, American. | Flower-buds of *Artemisia maritima*, var. *Stechmanniana*. (See *Chenopodium Oil*.) | 0.915–0.940 | −2 to −8 | | |
| Wormwood. | Green herb of *Artemisia absinthium* | 0.900–0.955 | | Dark green colour when distilled from green herb. Unpleasant odour. Markedly poisonous. Ref. ind. 1.466–1.475. | Thujone (free and as acetate); thujyl alcohol; phellandrene; pinene; cadinene; palmitic acid; acetic and isovaleric acids (as thujyl esters); a blue fraction. |
| Ylang-Ylang. | Flowers of *Cananga odorata.* | | | | Pinene; linalol; geraniol; *p*-cresol methyl ether; cadinene; eugenol; isoeugenol; cresol; linalyl and geranyl acetates and benzoates; benzyl alcohol; benzyl benzoate; methyl benzoate and salicylate; nerol; farnesol. |
| (Manila.) | Flowers of *Cananga odorata.* | 0.912–0.968 | −27 to −50 | 1.4747–1.494(30°) | |
| (Reunion.) | Flowers of *Cananga odorata.* | 0.930–0.967 | −34 to −65 | 1.500–1.510 | |
| Canaga (Manila.) | Flowers of *Cananga odorata.* | 0.906–0.952 | −27 to −87 | 1.4788–1.5082(30°) | |
| (Java.) | Flowers of *Cananga odorata.* | 0.906–0.956 | −15 to −52 | 1.4900–1.5050 | |
| Zedoary. | Root of *Curcuma Zedoaria.* | 0.982 to 1.012 | +8 to +18 | Viscid dark coloured oil. Distils at 240°–300°. Ind. ref. 1.502–1.506. | Cineole; sesquiterpene alcohol melting at 67°. |

## SOLUBILITY TABLE OF THE MOST USED ODORIFEROUS SUBSTANCES

### From Schimmel & Co's. Report

S. l. = less than 0.1 part per 100; ∞ = sol. in any proportion

| 100 parts by weight of solvent dissolve at 10° | 96% Alcohol | 70% Alcohol | Gly-cerol | Olive oil | Paraffin oil |
|---|---|---|---|---|---|
| Anethole | 20 | 3 | s. l.[1] | 10 | 6 |
| Anisic aldehyde (Aubépine) | ∞ [2] | 130 | 0.1 | ∞ | 1.5 (opal.) |
| Benzaldehyde | ∞ | 70 | 0.1 | ∞ | 7 |
| Benzoic acid ethyl ester | ∞ | 45 | s. l. | ∞ | 7 |
| Benzoic acid methyl ester | ∞ | 65 | 0.1 | ∞ | ∞ |
| Benzyl acetate | ∞ | 50 | 0.1 | ∞ | 13 |
| Benzyl alcohol | ∞ | ∞ | ∞ | ∞ | 1 |
| Benzyl benzoate | ∞ | 3 | s. l. | ∞ | 18 |
| Bornyl acetate | ∞ | 30 | s. l. | ∞ | ∞ |
| Cassia oil, artificial, Sch. & Co. (see Cinnamic aldehyde). | | | | | |
| Cinnamic aldehyde | ∞ | 30 | 0.1 | ∞ | 1.5 (opal.) |
| Cinnamic alcohol | ∞ | ∞ | 1 | 11 | 0.7 |
| Cinnamic acid benzyl ester | ∞ | 1.5 (cloudy) | s. l. | ∞ | 4(opal.) |
| Cinnamic acid ethyl ester | ∞ | 13 | s. l. | ∞ | ∞ |
| Cinnamic acid methyl ester | ∞ | 50 | s. l. | ∞ | ∞ |
| Cinnameïn (see Peru balsam oil). | | | | | |
| Citral | ∞ | 40 | s. l. | ∞ | ∞ |
| Citronellal | ∞ | 25 | s. l. | ∞ | ∞ (opal.) |
| Citronellol | ∞ | 55 | 0.1 | ∞ | ∞ |
| Coumarin | 8 | 4 | 0.1 | 1.5 | 0.3 |
| Eucalyptol | ∞ | 55 | 0.1 | ∞ | ∞ |
| Eugenol | ∞ | 110 | 0.1 | ∞ | 3 (opal.) |
| Geraniol | ∞ | 65 | 0.1 | ∞ | ∞ |
| Geranyl acetate | ∞ | 6 (cloudy) | s. l. | ∞ | ∞ |
| Geranyl methyl ether | ∞ | 6 (opal.) | s. l. | ∞ | ∞ |
| Heliotropin (Piperonal) | 8 | 5 | s. l. | 6 | 0.8 (opal.) |
| Hyacinth, Sch. & Co. | ∞ (opal.) | 3 (opal.) | s. l. | ∞ | 2 (opal.) |
| Isoeugenol | ∞ | 115 | 0.1 | ∞ | 0.7 (opal.) |
| Isosafrol | ∞ | 2 | s. l. | ∞ | ∞ |
| Jasmine, Sch. & Co. | ∞ | 150 | 0.1 | ∞ | 2 |
| Lilac, Sch. & Co. | ∞ | 65 | 0.1 | ∞ | ∞ |
| Lily of the Valley, Sch. & Co. | ∞ | 100 | 0.1 | ∞ | 4 |
| Linalol | ∞ | 50 | 0.1 | ∞ | ∞ |
| Linalyl acetate (Bergamiol) | ∞ | 24 | 0.1 | ∞ | ∞ |
| Menthol | 300 | 23 | 0.1 | 10 | 10 |
| Methylanthranilic acid methyl ester | ∞ | 7 | s. l. | ∞ | ∞ |
| Musk, artificial, Sch. & Co. | 0.5 | s. l. | s. l. | 2.5 | 0.7 |
| Musk, artificial, Sch. & Co., extra soluble | 1.1 | 0.2 | s. l. | 2.5 | 0.7 |
| Musk-seed (Ambrette) oil, Sch. & Co. | ∞ | 2 | s. l. | ∞ | ∞ |
| Muguet (see lily of the valley). | | | | | |
| Narcissus, Sch. & Co. | ∞ | 95 | 0.1 | ∞ | ∞ |
| Neoviolone 100% | ∞ | 40 | s. l. | ∞ | ∞ |
| Neroli, Sch. & Co. | ∞ | 35 | s. l. | ∞ | ∞ |
| Nerolin I | 5 | 0.8 | s. l. | 13 | 6 |
| Nerolin II | 2 | 0.4 | s. l. | 3 | 2 |
| Niobe oil (see Benzoic acid methyl ester). | | | | | |
| Novoviol | ∞ | 25 | s. l. | ∞ | ∞ |
| Orris oil, liquid, Sch. & Co. | ∞ | 6 | s. l. | ∞ | ∞ |
| Orris oil, solid | 10 | s. l. | s. l. | 2 | 0.8 |
| Paracresol methyl ether | ∞ | 10 | 0.1 | ∞ | ∞ |
| Peru balsam oil | ∞ | 1.5 (opal.) | s. l. | ∞ (opal.) | 0.7 (opal.) |
| Phenyl ethyl alcohol | ∞ | ∞ | 1.5 | ∞ | 1.5 |
| Pink blossom oil, Sch. & Co. | ∞ | 80 | 0.1 | ∞ | 1.5 (opal.) |
| Reseda-Geraniol, Sch. & Co. | ∞ | 50 | 0.1 | ∞ | ∞ (opal.) |
| Rose oil, artificial, Sch. & Co. | 20[1] | 20[1] | s. l. | 50 | 50 |
| Rose oil, artificial, liquid, Sch. & Co. | ∞ | 30[2] | s. l. | ∞ | ∞ |

## SOLUBILITY TABLE OF THE MOST USED ODORIFEROUS SUBSTANCES—Continued

| 100 parts by weight of solvent dissolve at 10° | 96 % alcohol | 70 % alcohol | Gly-cerol | Olive oil | Paraffin oil |
|---|---|---|---|---|---|
| Rose oil, natural, free from stearoptene............... | ∞ | 30 | s. l. | ∞ | ∞ |
| Safrole....................... | ∞ | 3 | s. l. | ∞ | ∞ |
| Salicylic acid amyl ester........ | ∞ | 1 | s. l. | ∞ | ∞ |
| Salicylic acid ethyl ester........ | ∞ | 7 | s. l. | ∞ | ∞ |
| Salicylic acid methyl ester...... | ∞ | 11 | 0. 1 | ∞ | ∞ |
| Santalol....................... | ∞ | 25 | 0. 1 | ∞ | ∞ |
| Terpineol, liquid............... | ∞ | 60 | 0. 1 | ∞ | ∞ |
| Thymene...................... | ∞ | 1 | s. l. | ∞ | ∞ |
| Thymol....................... | 200 | 30 | 0. 1 | 50 | 5 |
| Tréfol (see salicylic acid amyl ester). | | | | | |
| Vanillin....................... | 38 | 30 | 1 | 0. 9 | s. l. |
| Wallflower, Sch. & Co.......... | ∞ | ∞ | 0. 1 | ∞ | 0. 4 (opal.) |
| Wintergreen oil, artificial (see salicylic acid methyl ester). | | | | | |
| Ylang-Ylang, Sch. & Co........ | ∞ | 40 | s. l. | ∞ | ∞ |

[1] Soluble with strong separation of paraffin; completely soluble only when greatly diluted.
[2] Soluble with slight separation of paraffin; completely soluble only when greatly diluted.

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# RESINS

By ERNEST J. PARRY B. Sc., F. I. C.

The *resins* form a group of substances of very complex and variable chemical composition, but having somewhat similar physical characters. Any strict definition of a resin is impossible. These substances are, in general, brittle secretions of plant tissues, either normal or as the result of pathogenic conditions, sometimes artificially induced. They are insoluble in water, but more or less soluble in numerous organic solvents. They are amorphous (rarely crystalline), are fusible with more or less decomposition, and are sticky when heated, often at a comparatively low temperature.

Various substances or mixtures having the general physical characters of resins are obtainable artificially. Such are the artificial resins produced by formaldehyde condensation; of the "ester-gums" formed by condensing resins with glycerin.

The natural resins occur, as a rule, in exudations from plants, which exudations are sometimes normal and natural, and in other cases the result of diseases conditions. The exudation of these resinous products may often be induced artificially.

The resins sometimes occur naturally in admixture with gummy matter, essential oils, etc. Resinous products which contain much gum or allied substances—as is the case with asafœtida, galbanum, and ammoniacum—are called *gum-resins*. Similarly, such natural products as consist of solutions or emulsions of resins in essential. oils are called *oleo-resins*, or sometimes *balsams* or *turpentines*.

## CHEMICAL COMPOSITION OF RESINS

Even when separated from the gums, oils, and other substances with which they frequently co-occur in nature, the resins are rarely, if ever, pure chemical substances. They consist of a mixture of

numerous substances, the chemistry of which until recently was very obscure and still is of a very doubtful nature.

The resins were formerly regarded as oxidation-products of terpenes, but while this may be true of some of them, it is by no means a general rule. According to the researches of Doebner, certain resins are chiefly composed of condensation-products of aromatic aldehydes and phenols; but much of our knowledge of the chemistry of resins is chiefly due to the recent researches of A. Tschirch, who points out that the proximate constituents of resins, so far as they are known, may be classified under the following three heads; *Resin-esters* and their decomposition-products; *Resinolic* or *Resin Acids;* and *Resenes;* the last being substances of indifferent or unknown constitution. In many of the resins one or other of these classes preponderates, and the product consequently falls into the group of *ester-resins, acid resins,* or *resene-resins.* Representatives of all three classes are rarely present in the same product.

It must be remembered that in much of what follows, conclusions have been largely based on mere combustions of substances of which no crystalline derivatives have been prepared, so that formulæ assigned to given named substances may sometimes be nothing more than the empirical expression of the percentage composition of a mixture of resin constituents.

For the proximate analysis of resinous substances, Tschirch dissolves the sample in ether and agitates the solution successively with (1) 1% solution of ammonium carbonate; (2) 1% solution of sodium carbonate; (3) 0.1% solution of KOH and (4) 1% solution of KOH. These reagents dissolve the resin-acids, which can be precipitated from the alkaline liquids by a dilute mineral acid. On subjecting the ethereal solution to steam-distillation, and essential oil will volatilise, together with the ether. The residue may contain resin-esters and resenes, which can be separated by saponification with alcoholic potassium hydroxide, when the acid-radicals of the esters will form soluble potassium salts, and the resenes and resin-alcohols can be extracted by agitation with ether. The resin-alcohols can be acetylated or benzoylated, whereas most of the resenes resist such treatment.

Among the resins in which resin-esters predominate, Tschirch includes 1. The *benzo-resins*, gum-benzoin, Peru and Tolu balsams, storax, acaroid-resins, aloes resin, and dragon's blood; and 2. The

*umbelliferous gum-resins*, ammoniacum, galbanum, sagapenum, asafœtida, and umbelliferous opopanax.

The *terpeno-resins*, consisting chiefly of resin-acids, include the various coniferous resins, copaiba balsam, and the resin of Zanzibar copal.

The resinous materials in which *resenes* predominate include 1. The burseraceous oleo-resins, myrrh, olibanum, bdellium, burseraceous opopanax, Mecca balsam, various elemis, tacamahaca, and mastic; and 2. The dipterocarpus products, Doona resin, dammar, and Manila copal.

## Resin Esters

As a rule, the esters of the resins yield on saponification aromatic acids, such as benzoic and cinnamic acids. The following are the best known well defined of these aromatic acids.

**Benzoic acid,** $C_6H_5.COOH$, occurs in Peru and Tolu balsams, Siam benzoin, and (together with benzoyl-acetic and probably phenylhydracrylic acid) in dragon's blood.

**Cinnamic acid,** $C_6H_5.CH:CH.COOH$, is present in Peru and Tolu balsams, storax, yellow acaroid resin, and Sumatra benzoin.

**Salicylic acid,** $C_6H_3(OH).COOH$, has been found in gum ammoniacum.

**p-Coumaric acid,** $C_6H_4(OH).CH:CH.COOH$, is present in yellow and red acaroid resins.

**Ferulic acid,** $C_6H_3(OH).(OCH_3).CH.COOH$, occurs in asafœtida.

**Umbellic acid,** $C_6H_3(OH)(OH).CH:CH.COOH_3$, occurs together with its anhydride *umbelliferone*, in sagapenum, galbanum, and asafœtida.

## Resin Alcohols

The alcoholic constituents of the resin-esters were practically unknown until recently, but the researches of A. Tschirch and his collaborators have resulted in the isolation of the following resin-alcohols. Tschirch distinguishes two kinds of these—*resinols* and *resinotannols*. The members of the former group are colourless and give no tannin-reaction with iron salts, while the latter are coloured and give a tannin reaction.

The following are examples of resinols.

| Resinols | Occurrence | Formula | M. p. | Observers |
|---|---|---|---|---|
| α- and β-amyrin......... | Elemi............ | $C_{30}H_{49}(OH)$ | ............ | Vesterberg |
| Benzoresinol............. | Benzoin.......... | $C_{16}H_{25}(OH)O$ | 274° | Tschirch and Ludy. |
| Chironol............... | Burseraceous opo-panax. | $C_{23}H_{47}(OH)$ | 173° to 176° | Tschirch and Baur. |
| Pinoresinol............. | Pine resin........ | $C_{18}H_{18}O_6$ | 80° to 90° | Bamberger. |
| Storesinol.............. | Storax.......... | $C_{17}H_{30}O$ or $C_{36}H_{58}O_3$ | ............ | von Miller. |
| Succinoresinol............ | Amber.......... | $C_{12}H_{20}O$ | 275° | Tschirch and Aweng. |
| Succinoabietinol.......... | Amber.......... | $C_{40}H_{60}O_2$ | ............ | Tschirch and Aweng. |

A number of the best recognised resinotannols are given in the table on page 223.

In cases where such substances have been obtained, the products of acetylation and benzoylation of the resinotannols all contain one acetyl- or one bezoyl-group, with the exception of the product of benzoylation of aloresinotannol, which contains two benzoyl groups in the molecule.

## Resinolic Acids

These compounds are the characteristic free acids of resins, and also those in combination in various resins as esters, and are, in general, substances of complex constitution and high molecular weight. They usually contain one or more hydroxyl-groups as well as carboxyl-residues. Besides the many acids stated by Tschirch to exist in coniferous oleo-resins, the resin-acids tabulated on page 224 have been described.

Certain relations, more or less fanciful, can be traced between some of the resin-acids, by consideration of their reputed formulæ, which, however, must not, in most cases, be regarded as very positively ascertained.

Few of the resin-acids appear to contain more than one hydroxyl-group; but while sandaracolic and podocarpic acids contain only one carboxyl-group, two such groups appear to exist in the molecules of abietic, succino-abietic, trachylolic, and dammarolic acids.

TABLE OF RESINOTANNOLS

| Resinotannols | Occurrence | Formula | Acid product of treatment with nitric acid | Product of fusion with potassium hydroxide | Observers |
|---|---|---|---|---|---|
| Aloresinotannol | Cape aloes[1] | $C_{22}H_{26}O_4$. | .......... | .......... | Tschirch and Pedersen. |
| Ammoresinotannol | Ammoniacum | $C_{18}H_{29}O_2(OH)$. | Styphnic acid | Resorcinol | Tschirch and Luz. |
| Asaresinotannol | Asafœtida | $C_{21}H_{24}O_5$. | Picric acid | .......... | Tschirch and Polasek. |
| Dracoresinotannol | Palm dragon's blood. | $C_3H_2O(OH)$; or $C_{24}H_{20}O_4$. | .......... | .......... | Tschirch and K. Dieterich. |
| Erythroresinotannol | Red acaroid | $C_{40}H_{30}O_{10}$. | Picric acid | .......... | Tschirch and Hildebrand. |
| Galbanoresinotannol | Galbanum | $C_{18}H_{29}O_2(OH)$. | Camphoric and camphoronic acids. | .......... | Tschirch and Conrady. |
| Oporesinotannol | Umbelliferous opopanax. | $C_{12}H_{13}O_2(OH)$. | Oxalic and picric acids. | .......... | Tschirch and Knitl. |
| Panaxresinotannol | Burseraceous opopanax. | $C_{24}H_{49}O_7(OH)$. | | .......... | Tschirch and Baur. |
| Peruresinotannol | Peruvian balsam. | $C_{18}H_{10}O_4(OH)$. | Oxalic and picric acids. | .......... | Tschirch and Trog. |
| Sagaresinotannol | Sagapenum | $C_{24}H_{27}O_4(OH)$. | Styphnic acid | .......... | Tschirch and Hohenadel. |
| Siaresinotannol | Siam benzoin | $C_{12}H_{13}O_3(OH)$. | Picric acid | .......... | Tschirch and Lüdy. |
| Sumaresinotannol | Sumatra benzoin | $C_{48}H_{51}O_4(OH)$. | Picric acid | Protocatechuic acid. | Tschirch and Lüdy. |
| Toluresinotannol | Tolu balsam | $C_{17}H_{17}O_4(OH)$. | Oxalic and picric acids. | Protocatechuic acid. | Tschirch and Oberländer. |
| Xanthoresinotannol | Yellow acaroid | $C_{15}H_{46}O_{10}$. | Picric acid | .......... | Tschirch and Hildebrand. |

[1] Tschirch and Klaveness (*Arch. Pharm.*, 239, 241); have examined the resinotannol of Uganda aloes, the resin of which is a compound of *p*-coumaric acid with Uganda-resinotannol, $C_{21}H_{32}O_8$. This resinotannol is identical with that of Natal aloes.

## TABLE OF RESINOLIC ACIDS

| Resin acids | Occurrence | Formula | M. p.° | Observers |
|---|---|---|---|---|
| Agaric | | $C_{16}H_{30}O_5 + H_2O$ | 138 to 139 | Jahns. |
| Aleuritic | Shellac | $(C_{13}H_{26}O_4)n$ | 101.5 | Tschirch and Farner. |
| Shelloic | Shellac | $C_{15}H_{20}O_6$ | 199–201° | Harries and Nagel. |
| Callitrolic | | $C_{44}H_{62}O_5(OH).(COOH)$ | 248 | Tschirch and Balzer. |
| Copaivic[1] | Copaiba balsam | $C_{20}H_{34}O_2$ | …… | T. A. Henry. |
| Dammarolic | Dammar | $C_{20}H_{36}O_2$ | …… | Schweitzer. |
| Guaiacic | Guaiacum | $C_{44}H_{77}O_3(OH).(COOH)_2$ | …… | Tschirch and Glimmann. |
| Guaiaconic | Guaiacum | $C_{20}H_{24}O_4$ | 75 to 80 | Döbner and Lücker. |
| Illuric | African copaiba | $C_{20}H_{34}O_6$ | 95 to 100 | Döbner and Lücker. |
| Pimaric (inactive) | Sandarac | $C_{20}H_{30}O_2$ | 128 | Tschirch. |
| Podocarpic | Podocarpin resin | $C_{17}H_{22}O_3$ | 171 | T. A. Henry. |
| Sandaracolic | Sandarac | $C_{43}H_{61}O_3(OCH_3)(OH)(COOH)$ | 187 to 188 } 140 } (152) | Oudemans. Tschirch and Balzer. |
| Succinoabietic (a) | Amber (succinite) | $C_{20}H_{30}O_4$ | 122 | Tschirch and Aweng. |
| Succinoabietic (b) | Amber (gedanite) | $C_{19}H_{28}O_4$ | 120° | Tschirch and Aweng. |
| Succino abietinolic | Amber (both varieties) | $C_{20}H_9O_5$ | …… | Tschirch and Aweng. |
| Succino silvinic | Amber (both varieties) | $C_{24}H_{36}O_2$ | 104° | Tschirch and Aweng. |
| Trachylolic | Zanzibar copal | $C_{46}H_{88}O_8$ | 165 | Tschirch and Stephan. |
| Iso-trachylolic | Zanzibar copal | $C_{66}H_{98}O_8$ | 105 to 107 | Tschirch and Stephan. |
| Elemic | Elemi | $C_{36}H_{46}O_4$ | …… | Flückiger. |
| Boswellic | Olibanum | $C_{32}H_{52}O_4$ | 142 to 150 | Tschirch and Halbey. |
| Chironolic | Burseraceous opopanax | $C_{28}H_{44}O_4$ | 100 to 108 | Tschirch and Baur. |
| α-Masticic | Mastic | $C_{23}H_{36}O_4$ | 90 to 91 | Tschirch and Reutter. |
| β-Masticic | Mastic | $C_{23}H_{36}O_4$ | 89.5 to 90.5 | |
| Masticolic | Mastic | $C_{23}H_{36}O_4$ | 201 | |
| α-Masticonic | Mastic | $C_{22}H_{48}O_4$ | 96 to 96.5 | |
| β-Masticonic | Mastic | $C_{22}H_{46}O_4$ | 91 to 92 | |

[1] Meta- and oxy-copaivic acids, and probably also several isomeric copaivic acids, are said to occur in the different varieties of copaiba.

## Resenes

These substances are practically unclassifiable. They are oxygenated compounds, but are not acted on by alkalies and possess no characteristic chemical properties. They do not appear to be alcohols, esters, acids, ketones, or aldehydes. They are insoluble in and unacted on by alkali hydroxides, a fact which gives the resins containing them one of their chief values for the manufacture of varnishes. The following are among the resenes which have been described by Tschirch and his co-workers:

| Resene | Occurrence | Formula | M. p. ° | Observers |
|---|---|---|---|---|
| Alban.............. | Gutta-percha... | (?) $C_{40}H_{64}O_2$. | 195 | Tschirch and Oesterle. |
| α-Copalresene.......... | Copal......... | (?) $C_{25}H_{38}O_4$. | 75 to 77 | Tschirch and Stephan. |
| β-Copalresene.......... | Copal......... | $C_{21}H_{30}O_4$. | ...... | Tschirch and Stephan. |
| α-Dammarresene........ | Dammar....... | (?) $C_{33}H_{52}O_2$. | 65 | Tschirch and Glimmann. |
| β-Dammarresene........ | Dammar....... | $C_{21}H_{32}O$. | 206 | Tschirch and Glimmann. |
| Dracoalban........... | Palm Dragon's blood. | $C_{30}H_{40}O_4$ | ...... | Tschirch and K. Dieterich. |
| Dracoresene........... | Palm Dragon's blood. | (?) $C_{24}H_{44}O_2$. | 74 | Tschirch and K. Dieterich. |
| Fluavil............... | Gutta-percha... | (?) $C_{40}H_{64}O_4$. | ...... | Tschirch and Oesterle. |
| Gurjunresene.......... | Gurjun balsam.. | $C_{17}H_{28}O_2$. | ...... | Tschirch and Weil. |
| Myroxoresene.......... | Fruit of myroxylons. | $C_7H_{10}O$. | ...... | Tschirch and Germann. |
| α-Masticoresene........ | Mastic......... | $C_{33}H_{56}O_4$. | 74 to 75 | Tschirch and Reutter. |
| β-Masticoresene........ | Mastic......... | ............. | ...... | Tschirch and Reutter. |
| Olibanoresene.......... | Olibanum...... | $(C_{14}H_{22}O)n$. | 62 | Tschirch and Halbey. |
| α-Panaxresene......... | Burseraceous opopanax. | $C_{33}H_{44}O_4$. | ...... | Tschirch and Baur. |
| β-Panaxresene......... | Burseraceous opopanax. | $C_{33}H_{52}O_5$. | ...... | Tschirch and Baur. |

# GENERAL CHARACTERS OF RESINS

The resins as a class are solid, more or less transparent, brittle substances, and in rare cases are capable of crystallising. They have usually no marked odour or taste, and vary in sp. gr. from 0.90 to 1.25. The resins are easily fusible, but not volatile without decomposition and are decomposed when heated in close vessels, yielding empyreumatic products consisting chiefly of hydrocarbons. Heated in the air, the resins burn readily with a smoky flame. They are very bad conductors of electricity, and when rubbed become negatively electrified.

The resins are insoluble in water, but are soluble to a great extent in alcohol and many other organic solvents. In most cases the solutions are acid, to an extent depending on the nature of the resin,

and when treated with an alkali yield a lather. The solutions of the resins in alkalies differ from ordinary soap solutions in the fact that they cannot be "salted out" by the addition of common salt, unless this be used in very large quantity.

## Commercial Resins

Many of the resins are important articles of commerce. A number of them are used to an enormous extent for the manufacture of varnishes and in certain branches of soap-making. They are also employed in the manufacture of sealing-wax, for hat-stiffening, for incense, and to a certain extent in medicine.

In the examination of resins, the following general principles should be observed. Frequently it is not necessary to examine a resin in so full a manner as the following processes involve, but in many cases nothing but a full examination will give reliable information as to the purity of the product.

*Water* and certain *general impurities* may be separated from the resins by dissolving them in oil of turpentine, or other suitable solvent. If the operation be conducted in a graduated tube, the separated water may be measured and the insoluble matter filtered off, washed with the solvent, dried, weighed, and further examined. The residue thus obtained will often, especially in the case of medicinal resins, be found to consist of woody fibre.

From the *neutral fixed oil*, resins may be separated by treating the mixture with alcohol of about 0.85 sp. gr. The alcohol is subsequently separated, and the dissolved resin recovered by evaporating it to dryness. The results are only approximately correct. Acid resins, such as common colophony, may be separated from the neutral fats by boiling the substance with a strong solution of sodium hydrogen carbonate or borax. After cooling, the aqueous liquid is separated from the oil, and the resin precipitated from its solution by adding hydrochloric acid. Methods of separating resin from fatty acids are described under "Colophony."

Resins may be separated from the *essential oils*, in admixture with which they so frequently occur, by distilling the substance in a current of steam, and then, if necessary, immersing the flask or retort in a calcium chloride bath, while still continuing the current of steam.

Essential oils may also be separated by rubbing down the resinous substance to a fine powder in admixture with a known quantity of sand, and then macerating in petroleum spirit. Part of the true resin will also be dissolved, and hence the filtered solution must be evaporated to dryness, the residue heated to 110° or 120° until constant in weight, and the weight found added to that of the undissolved portion, when the loss will be the essential oil and other volatile constituents. The amount of resin dissolved by the petroleum spirit is often of interest. Thus, in the case of copal, the quality of the sample is better, the smaller the quantity of non-volatile matter dissolved by the petroleum spirit. The mixture of ethereal oil and resin left on evaporating the petroleum spirit at the ordinary temperature often yields more or less characteristic colour-reactions.

The residue insoluble in petroleum spirit should be weighed and then treated with ether, after which it should be ascertained if alcohol will extract anything insoluble in ether or petroleum-spirit. In the case of gum-resins, *sugar* is one of the principal substances extracted by alcohol, while gum, salts, etc., may subsequently be dissolved out by water, which in some cases (*e. g.*, gum tragacanth) may produce swelling without actual solution of the gummy matter. The ethereal solution should be tested as to its miscibility with alcohol, and a portion may be evaporated to dryness and the residue examined by colour-tests. It is also desirable to ascetain if a turbidity is produced by adding ether, ammonia, or an alcoholic solution of lead acetate to the spirituous solution of the original resin.

Mauch recommends the treatment of the substance with about 15 times its weight of a 60% solution of chloral hydrate in water. The liquid is filtered from woody fibre or other insoluble matter and the filtrate mixed with 10 parts of alcohol of 95%. This precipitates the gummy matters in a convenient condition for filtration and weighing, while the resinous matters and essential oils remain in solution.

Useful information may also be obtained by treating the original resin with chloroform, ether, or a saturated aqueous solution of sodium carbonate; the last may produce colorations or dissolve out cinnamic acid and acid resins.

Various observers have applied to resins the methods which have been found so valuable in the examination of fatty and essential oils, and the acid values, saponification values, ester values, etc.,

have been determined. Karl Dieterich has devoted much time and attention to the investigation of this subject. The resins are complex substances; consequently their analysis is a matter of some difficulty. One general method equally applicable to all classes of resins cannot be adopted, and selected methods suitable for the material under examination must be applied.

**Acid Value.**—(*a*) Direct titration in alcoholic solution with alcoholic potassium hydroxide.

(*b*) For certain resins, free from esters, Dieterich has proposed his so-called indirect method. The resin is allowed to stand for 24 hours with excess of alkali, and is then titrated back with standard sulphuric acid. Although this cannot be considered a true acid value it has been found to give constant results, and can be considered as a legitimate method for determining a certain constant value. This figure is of doubtful value. Few resins are quite free from esters, which will be, to some extent, decomposed by this treatment. Further, many resins contain lactones which are only slowly converted into acids by contact with alkali; so that this figure will include lactones and some esters.

(*c*) Marcusson and Winterfeld have recently proposed a new method for estimating the acid value. The resin is boiled with a solvent containing equal parts of absolute alcohol and benzene. They have found this a very suitable method for estimating the acid value of all the copals, dammar, sandarac, etc., and have obtained the following results:

| Resin | Acid value | Resin | Acid value |
|-------|------------|-------|------------|
| Zanzibar copal......... | 72.4 | Amber (spurious)....... | 14.5 |
| Kauri copal........... | 65.6 | Mastic............... | 60.2 |
| Manila copal......... | 141.8 | Sandarac............. | 137.7 |
| Amber (mined)........ | 26.7 | Dammar.............. | 24.8 |
| Amber (beach)........ | 33.1 | Elemi (soft).......... | 15.2 |

**Saponification Value.**—This value can be estimated in the ordinary way. Dieterich has also used hot, cold, and fractional saponification, but these values have as yet practically no value for commercial analysis. The *acetyl value* (*Dieterich, Helfenberger Annalen*, 1897, 35) of resins (having the same significance as in the analysis of fatty oils) has occasionally been estimated, as have the *carboxyl values.* (*Kitt, Chem. Ztg.*, 1898, 358.)

The following table gives the results obtained by G. Gregor and by Bamberger for the *methoxyl-value* (*Oest. Chem. Zeit.*, 1898,

## METHOXYL-VALUES OF RESINS

| No. | Description of resin or balsam | Methoxyl-value | | | |
|-----|-------------------------------|------|------|------|------|
|     |                               | Gregor | | Bamberger | |
| 1   | Aloë hepatica.................... | 4.2 | ...... | 3.9 | ...... |
| 2   | Aloë lucida.:.................... | 0 | ...... | 0 | ...... |
| 3   | } Ammoniacum................... { | 8.6 | ...... | 11 | ...... |
| 4   |                               | 9 | ...... | ...... | ...... |
| 5   | } Asafœtida..................... { | 11.9 | ...... | 18 | ...... |
| 6   |                               | 6.9 | ...... | ...... | ...... |
| 7   | Gum benzoin, Siam............... | 43.4 | 4.3 | 30 | 28.5 |
| 8   |                               | 25.5 | 25.3 | 16.5 | 16.2 |
| 9   | } Gum benzoin, Sumatra........... { | 20.3 | ...... | ...... | ...... |
| 10  |                               | 20.1 | ...... | ...... | ...... |
| 11  | Benzoin (almond), Sumatra.......... | 20 | ...... | 13.3 | ...... |
| 12  | Canada balsam.................... | 0 | ...... | 0 | ...... |
| 13  | Copaiba balsam................... | 0 | ...... | 0 | ...... |
| 14  | Copal........................... | 0 | ...... | 0 | ...... |
| 15  | Colophony....................... | 0 | ...... | 0 | ...... |
| 16  | Dammar......................... | 0 | ...... | 0 | ...... |
| 17  | } Dragon's blood.................. { | 27.6 | ...... | 33.8 | ...... |
| 18  |                               | 25.3 | ...... | ...... | ...... |
| 19  | } Euphorbium.................... { | 0 | ...... | 0 | ...... |
| 20  |                               | 2.8 | ...... | 0 | ...... |
| 21  | } Elemi......................... { | 0 | ...... | 0 | ...... |
| 22  |                               | 2.5 | ...... | ...... | ...... |
| 23  | Pine resin....................... | 0 | ...... | 0 | ...... |
| 24  | Galbanum........................ | 3.7 | ...... | 3.7 | 4 |
| 25  | } Gamboge...................... { | 0 | ...... | 0 | ...... |
| 26  |                               | 2.4 | ...... | ...... | ...... |
| 27  | Guaiacum........................ | 73.8 | 74.2 | 83.8 | 84.0 |
| 28  | Gurjun balsam.................... | 0 | ...... | ...... | ...... |
| 29  | Jalap resin....................... | 0 | ...... | 0 | ...... |
| 30  | Labdanum........................ | 0 | ...... | 0 | ...... |
| 31  | } Liquidambar styrax.............. { | 4.5 | ...... | 0 | ...... |
| 32  |                               | 3.6 | ...... | ...... | ...... |
| 33  | Myrrh........................... | 13.5 | ...... | 13.6 | 13.2 |
| 34  | } Gum mastic.................... { | 0 | ...... | 0 | ...... |
| 35  |                               | 1.9 | ...... | ...... | ...... |
| 36  | Olibanum........................ | 6.4 | ...... | 5.3 | ...... |
| 37  | } Balsam of Peru................. { | 16.7 | ...... | 14.4 | ...... |
| 38  |                               | 21.8 | 21.7 | ...... | ...... |
| 39  |                               | 22.6 | ...... | ...... | ...... |
| 40  | Scammonium..................... | 0 | ...... | 0 | ...... |
| 41  | Sandarac........................ | 0 | ...... | 0 | ...... |
| 42  | Venice turpentine................. | 0 | ...... | 0 | ...... |
| 43  | } Balsam of Tolu................. { | 41.6 | ...... | 46.8 | ...... |
| 44  |                               | 41.7 | ...... | ...... | ...... |

## APPROXIMATE ANALYTICAL CONSTANTS OF RESINS

| Substance | Source or variety | Acid value | Ester value | Iodine absorption | Ash |
|---|---|---|---|---|---|
| **Resins.** | | | | % | % |
| Amber | *Pinites Succinifer* | 15–35 | 70–95 | 62.1 | 0.28 |
| Anime | Various | 33; 34 | 74; 91 | | 0.05 to 0.11 |
| Caoutchouc | | 18 to 27 | 47 to 62 | 128 to 137 | |
| Colophony | Residue from turpentine distillations, *Pinus* species | 81 | | 71 | |
| Copal | *Trachylobium, Hymenæa* and other species | 146 to 178 | 7 to 20 | 118 to 128 | 0.05; 0.02 <br> 0.08; 1.20 |
| Dammar | *Dammara, Hopea* and other species | 50 to 135 | 30–80 | 74 to 170 | trace to 2.06 |
| | | | 35 to 85 | | |
| | Batavia | 33 to 72 | 0 to 2 | 63.6 | 0.03 to 0.07 |
| | Various | 21 to 27 | 4 to 20 | 130 to 142 | 0.01 |
| Dragon's Blood | *Dæmonorops Draco* and *Dracæna Cinnabari* | 22 | 14 | 117.7 | 3.58 |
| Elemi | *Canarium* species | 15 to 34 | 142 | 98.4 | |
| | Manila | 11 | 7 to 35 | 72.4 | |
| Guaiacum | *Guaiacum officinale* | 15 to 28 | 24 | 85.1 | |
| Jalap | *Ipomœa purga* | 46 to 53 | 121 to 139 | | |
| | | 12 to 16 | 120 | | |
| Jalapin | Jalap resin | 15 to 27 | 110 to 130 | | |
| Mastic | *Pistacia lentiscus* | 50 to 56 | 23 | 159 | 0.14 to 0.20 |

| | | | | | |
| --- | --- | --- | --- | --- | --- |
| Sandarac | *Callitris quadrivalvis* | 90 to 154 | 1 to 11 | 134.3 | 0.04 to 0.17 |
| | | 141 | 33 | 66.8 | |
| **Oleo-resins** | | | | | |
| Canada balsam | *Abies balsamea* | 81 to 87 | 5 to 10 | | |
| Gurjun balsam | | 10 to 25 | 4.5 to 9.0 | | |
| Mecca balsam | *Balsamodendron gileadense* | 40 to 52 | 1 to 10 | | |
| Common turpentine | *Pinus Sylvestris, P. Cembra, Abies species, etc.* | 108 to 145 | 101.4 | | |
| Chian turpentine | | 48; 53- | 3 to 60.2 | | |
| Venice turpentine | | 65 to 75 | 19 to 21.50 | 145 to 155 | |
| Burgundy pitch | | 135 to 148 | 30 to 55 | | |
| **Gum-resins** | | | | | |
| Ammoniacum | *Dorema Ammoniacum.* | | | | |
| Asafœtida | *Ferula species* | 60 to 80 | 19 to 38 | | |
| Bdellium | *Various Burseraceœ.* | 11 to 82 | 82 to 182 | | |
| Euphorbium | *Euphorbia resinifera.* | 10 to 37 | 47 to 96 | | |
| Galbanum | *Peucedanum species.* | 13 to 25 | 49 to 68 | | |
| Gamboge | *Garcinia Morella.* | 20–40 | 60 to 90 | 115.8 | 0.48 |
| | | 81 | 67 | | |
| | | 100 | 57 | | |
| Myrrh | *Herabol-Myrrh.* | 64 to 70 | 95 to 146 | | |
| | | 25 | 204 | | |
| | *Indian.* | 42 | 131 | | |
| Olibanum | *Boswellia species.* | 45 to 88 | 7 to 72 | | |
| | *Indian.* | 50 | 60 | | |

Nos. 8 and 9) of various resins and balsams. Gregor's modification of Zeisel's method was employed in each case. These figures have as yet only a limited value analytically.[1]

The acid and ester values in the table which follows represent the numbers of mg. of KOH absorbed by 1 grm. of the sample, and were obtained in the usual manner, except in the case of the gum-resins, when the titration was effected in the following way (A. Kremel; E. and K. Dieterich):

1 grm. of the gum-resin was mixed with powdered gypsum and extracted with 95% alcohol. The residue from the evaporation of the alcoholic extract (which gives the percentage of resin) was then redissolved in 50 c.c. of alcohol, one-half of the liquid being used for the acid estimation and the other half for the esters. The amount of KOH used was then calculated to 1 grm. of the pure resin. The method followed by von Schmidt and Erban for the estimation of the amount of iodine absorbed was to dissolve 1 grm. of the pure resin in hot alcohol, when, after cooling the liquid, the iodine solution was added in excess. The mixture was allowed to stand for twenty-four hours before titration. The figures in the table marked with an asterisk were obtained on that portion of the resin soluble in alcohol, the insoluble matter being separated. The remaining iodine-absorption figures of von Schmidt and Erban (not marked by an asterisk) were obtained on the alcoholic solution in presence of the insoluble residue.

The figures in the table on page 233, obtained by the analysis of resins used in the manufacture of spirit-varnishes, are due to A. Rudling (*Chem. Rev. Fett. u Harz. Ind.*, 1903, **10**, 51). Those referring to shellac are omitted owing to the obvious impurity of some of the samples examined. The figures in columns A were obtained with the crude resins; in B with the dry samples after being freed from mechanical impurities. Columns C refer to the alcoholic extract after drying at 100°.[2]

The foregoing methods afford valuable indications of the nature of resinous substances, but the positive identification of the various

[1] The figures for *shellac* have been omitted from the table, since most of the samples examined were obviously adulterated. All the reliable data with reference to this resin will be found under shellac.

[2] In these analyses, the iodine value was estimated by dissolving 0.5 to 1.0 grm. in 25 c.c. of alcohol with 10 c.c. of chloroform, and titrating after 6 hours. The saponification value was estimated by boiling 1 grm. of the resin for 15 mins. with 25 c.c. of potassium hydroxide solution under a reflux-condenser, then diluting the liquid with 100 c.c. of alcohol, and titrating with standard acid; and the acid value by boiling 1 grm. of resin for 5 mins. under a reflux condenser with 100 c.c. of 90% alcohol, and titrating the liquid when cold

ANALYTICAL CONSTANTS OF RESINS (A. Rudling)

| Resin | Water % | Substance insoluble in alcohol % | Iodine value | | | Saponification value | | | Acid value | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | A | B | C | A | B | C | A | B | C |
| Yellow acaroid (xanthorrhea) resin | 5.65 | 0.93 | 176.2 | 188.6 | 160.0 | 98.0 | 104.9 | 106.0 | 82.3 | 88.1 | 64.0 |
| Yellow acaroid resin (Adelaide) | 4.50 | 3.52 | 176.2 | 191.5 | 160.0 | 100.8 | 109.5 | 106.0 | 67.2 | 73.0 | 67.0 |
| Yellow acaroid resin (Victoria) | 4.40 | 0.88 | 175.0 | 184.7 | 160.0 | 156.8 | 165.5 | 176.4 | 72.8 | 76.8 | 84.0 |
| Red acaroid resin | 4.90 | 5.26 | 164.5 | 183.1 | 156.7 | 64.4 | 71.7 | 106.0 | 18.5 | 20.6 | 25.0 |
| Sandarac | 2.00 | 0.54 | 91.8 | 94.2 | 98.7 | 152.4 | 166.7 | 170.8 | 137.2 | 140.8 | 137.8 |
| Manila (spirit soluble) | 2.10 | 2.30 | 106.0 | 110.8 | 91.0 | 187.6 | 196.2 | 187.6 | 136.6 | 142.8 | 150.0 |
| Manila (hard) | 1.68 | 3.39 | 86.0 | 90.6 | …… | 215.6 | 227.1 | …… | 138.9 | 146.3 | …… |
| White French resin | 0.80 | 0.10 | 137.1 | 138.3 | …… | 177.8 | 179.4 | …… | 169.7 | 171.2 | …… |
| American resin | 0.75 | 0.20 | 122.0 | 123.2 | …… | 182.0 | 183.8 | …… | 157.9 | 159.4 | …… |
| Venetian turpentine (genuine) | …… | …… | 148.5 | …… | …… | 121.8 | …… | …… | 73.9 | …… | …… |
| Venetian turpentine (spurious) | …… | …… | 109.6 | …… | …… | 117.6 | …… | …… | 103.0 | …… | …… |
| Elemi | 0.2 | 0.1 | 83.6 | 83.8 | …… | 28.0 | 28.0 | …… | 22.4 | 22.4 | …… |

individual resins of commerce is a matter of considerable difficulty even when only one is present, and in admixture the task is often insuperable.

This conclusion is emphasised by the fact that in the manufacture of varnishes, the resins are usually heated together with oil or other substances to a temperature of about 300°. The effect of such heating is exemplified by various figures given by J. Lewkowitsch (*Analyst*, 1901, **26**, 38). From his results it appears that not only do different commercial samples of presumably similar nature and origin give very varying figures, but the effect of heat on a given sample is often such as to destroy the informative value of any analytical characters it may yield. It is desirable to place the results on record, but it is evident that at present in many cases any conclusion as to the origin or purity of a resin, from the figures obtained by its analysis, must be drawn with the greatest caution.

## RESINS

### ACAROID RESINS

**Occurrence.**—Red and yellow acaroid resins are the products of various species of *Xanthorrhœa*, especially of *X. Australis*, plants found over a wide area of the Australian continent. In addition to the Australian gums, a red West Indian variety is also known.

The red resin is commonly known in Australia as "grass-tree gum." The yellow variety is often termed Botany Bay gum, and comes principally from Tasmania. According to Umney (*Perfumery and Essential Oil Record*, 1915, 212) the pale variety of the resin obtained from New South Wales is obtained from *X. Hastilis* and the dark variety from *X. Arborea*. The former is the more aromatic, and is of particular interest because it contains an appreciable amount of benzoic acid. It has a certain amount of value for perfumery, and can be used as a cheap substitute for benzoin, storax or tolu. On burning, it emits a fragrant odour and might be employed as an incense resin. It contains from 4.6 to 7.2% of benzoic acid.

When heated with nitric acid it yields much picric acid. An interesting account of the method of collecting the resin is given in the (*Pharm. Jour.*, **XXI**, 906). The stems of the "grass trees" are chopped down, broken up into convenient pieces and allowed to fall onto a sheet. A stout stick or a flail completes the work of

disintegration. The substance is then passed through a sieve, the woody portions being thus removed, and what has passed through the sieve is easily winnowed by a gentle breeze and the granules of "gum" are collected.

L. E. Andés (*Chem. Rev. Fett Harz. Ind.*, 1909, **16**, 160) gives the following interesting account of these resins. Of the various species of *Xanthorrhœa*, *X. Drummondii*, a West Australian plant, is reported to yield the most resin. *X. Tateana* (S. Australia, Kangaroo Island) furnishes a ligneous, vesiculated, readily friable and odourless resin. The mass is dark red; the powder is yellowish and imparts a blood red colour to hot water. Petroleum spirit extracts 1% of a colourless, odourless resin; strong alcohol dissolves it entirely, forming a deep red solution, which deposits crystals of benzoic acid on evaporation. *X. Hastitis* (New South Wales and Queensland) produces a resin of sweetish odour, resembling that of benzoin; it is readily friable, the powder resembling gamboge and undergoing change of colour when exposed to light. It melts in boiling water, rendering the liquid turbid and yellow. Petroleum spirit extracts 1% of a pleasant smelling substance; alcohol dissolves 94%, and the solution yields crystals of benzoic acid on evaporation. The purified resin melts at 97–98°. *X. Arborea* (New South Wales and Queensland) furnishes compact pieces mixed with leaves: the colour of the product varies from purple brown to carmine red. It forms a readily friable powder, of the colour of raw sienna, and tastes like benzoin. Petroleum spirit extracts 8%, and alcohol 92%. The alcoholic extract deposits crystals of benzoic acid on evaporation, but in less quantity than the other resins. *X. Australis* (Tasmania and Victoria) affords irregular-shaped spheroidal masses of a friable resin of dark red colour, resembling Dragon's blood. Its alcoholic solution is clearer than those of any of the other Xanthorrhæa resins.

**Chemical Composition.**—According to K. Hildebrand, the composition of red and yellow acaroid resins is very similar, the main distinction being the presence of cinnamic acid in the latter kind. In the red resin, which is chiefly the product of *X. Australis*, he found 1% of free $p$-coumaric acid, and 2% of this acid as an ester of erythro-resinotannol, $C_{40}H_{39}O_9.OH$; traces of benzoic acid also in combination; and traces of $p$-hydroxybenzaldehyde. About 85% of the resin consists of the $p$-coumaric acid ester and the resin alcohol. The yellow resin contains about 4% of free $p$-coumaric acid and a small

quantity of free cinnamic acid.    Both acids, chiefly the former, are
present in the form of esters of xantho-resinotannol, $C_{48}H_{45}O_9.OH$,
and these substances form the principal portion of the resin.    In
addition, traces of several compounds which have not been definitely
identified are also present.    These probably consist of styracin,
phenyl-propylcinnamate, $p$-hydroxybenzaldehyde, and vanillin.

Uses.—These resins are used in the manufacture of sealing-wax,
the preparation of spirit lacquers for coating metals, especially the
brass parts of scientific instruments, to a small extent in medicine,
and the darker varieties, when dissolved in alcohol, make an excel-
lent mahogany stain for wood.    The acaroid resins when dissolved
are fast to light, consequently they are in some cases preferable to
dragon's blood as colouring media.    The alkaline solutions of these
resins can be used for sizing paper.

Adulterants.—Owing to the low price at which these resins are
sold, they are not adulterated, but are frequently used to adulterate
the more expensive resins.

General Properties.—Yellow acaroid resin occurs mostly in long
or round pieces of a red-brown colour, which possess an odour resem-
bling that of benzoin.

Red acaroid resin (Australian), the so-called "grass-tree gum," is
found in large and small uneven pieces of a brownish colour, often
mixed with sand and other impurities; thin pieces when examined by
transmitted light show a ruby-red colour.    It differs from yellow
acaroid, or "Botany Bay gum," in not giving a cinnamic acid reaction.
According to Maiden, only about 2% of the yellow acaroid resin is
soluble in petroleum spirit, and as much as 90 to 95% in alcohol.
Red acaroid resin, however, yields as much as 3% to petroleum spirit.

Red Acaroid Resin (West Indian).—This resin from the Bahamas
presents the appearance and character of the red commercial variety.
It is light in colour, quite soluble in alcohol, and yields only about
3% of ash.    The composition appears to agree very closely with that
of the Australian resin, although, unlike the latter, it yields cinnamic
acid on treatment with alkaline solutions.    West Indian acaroid can
be used for the same purpose as the Australian varieties, except that
its light colour would preclude its use as a stain.    Para-coumaric
acid is present in most acaroid resins.

Identification and Analytical Data.—H. Rebs (*Lack- und Farben-
Ind.*, 1908, No. 11) has described the following method for identifying

acaroid resin in the presence of manila, shellac, sandarac, and colophony. A small amount of the material under examination is heated with 10 to 20 drops of nitric acid until nitrous fumes are copiously evolved. When cold, the residue is dissolved in alcohol, and 10 to 20 drops of a 5% ferric chloride solution are added to the intensely red liquid. A brown to brownish-black coloration accompanied by a cloudy appearance in the liquid, denotes the presence of gum acaroid. By this means 1% can easily be detected.

Schimmel & Co. give 4.9 as the acid value and 69.4 as the ester value of a sample of oil from the yellow resin. Rudling examined various samples of these resins, and the values obtained by him are given on page 233. An essential oil distilled from yellow acaroid obtained from *X. Hastilis* was an oil of storax-like odour having a sp. gr. of 0.937 and an optical rotation of $-3° 14'$. The saponification value of the oil was 74.3, and the acid value 4.9, showing the presence of a large proportion of esters. The free acid was identified as cinnamic acid which was also found in the esters. From the low boiling fraction styrene was isolated. The oil from the resin of *X. Australis* has the following characters:

> sp. gr. 0.963; acid value 47.6; ester value, 37.5. It is optically inactive.

The oil from a yellow resin derived from *X. Tateana* contains pæonol, and hydroxypæonol. A similar oil is yielded by *X. Preusii.*

Haensel (*Apoth. Zeit.*, 1908, **23,** 279) has described acaroid resin oil as an optically inactive reddish-brown liquid with an odour recalling Tolu balsam. It has a sp. gr. 0.960, an acid value 47.6, and ester value 37.5. When treated with a solution of sodium hydroxide, 1.94% of cinnamic acid and 7.6% of a yellowish resin are removed. The washed oil when saponified gives a further yield of cinnamic acid and resin. Styrene is also present in the oil.

## AMBER

**Occurrence.**—Amber is a fossil resin derived from *Pinites succinifer*.

**Commercial Varieties.**—A number of varieties are known commercially, but, according to Helm and Potonic (*Ph. C.*, 1890, 744), the following kinds should be regarded as distinct:

1. Succinite, the most important variety, and the one that is generally specified under the name amber, forms yellow or yellowish-brown masses which are often quite transparent or semi-transparent, but sometimes so milky as to be quite opaque. It melts at 250°–300°.

2. Gedanite, also known as "soft amber," is a pure yellow, transparent variety which swells at 140° to 180° and melts on further heating. It is said to contain less succinic acid than ordinary amber.

3. Glessite, usually brown and opaque.

4. Stantienite or black resin, a brittle variety.

5. Beckerite, a brown opaque resin.

**Imitation Amber.**—This product is manufactured to a certain extent from the shavings of amber produced when the pieces are trimmed. Very strong pressure is used, and although the resin is all genuine amber, the peculiar method of aggregation of its particles causes it to differ in its physical properties from natural amber, so that the term "spurious amber" appears to be justifiable. Sometimes, however, colophony and others resins are worked in.

**Chemical Composition.**—The most recent examination of the chemical characters of amber resin is that of Tschirch, Aweng, de Jong and Hermann (*Helv. Chim. Acta*, 1923, **6**, 214–225). A comparison was made between the constituents of the two forms of amber, succinite and gedanite.

The finely crushed resin was first extracted with alcohol, and the unextracted matter dissolved in ether. The alcohol-soluble resin was then extracted with petroleum spirit. The spirit solution was extracted with an aqueous solution of carbonate of ammonia; two entirely different acids were obtained, for which the authors have, unfortunately, retained the same name, succinoxyabietic acid. The acid obtained from succinite melted at 122° and has the composition $C_{20}H_{30}O_4$. That yielded by gedanite melted at 120° and has the composition $C_{19}H_{28}O_4$. It is possible that the former is the methyl derivative of the latter. They are both monobasic acids, and are only present to the extent of about 0.5% in the amber.

By again extracting the ethereal solution with a solution of sodium carbonate another acid was obtained, having the formula $C_{40}H_{60}O_5$. This acid is monobasic and has been named succinoabietinolic acid. It is present in both forms of amber to the extent of about 12%. All

three acids appear to be formed by the autoxidation of resin acids of the type of abietic acid $C_{20}H_{30}O_2$.

The extract by petroleum spirit was examined by extracting with a $5\%$ solution of sodium hydroxide. The aqueous solution was separated and the petroleum spirit residue was found to contain an alcoholic substance which has been named succinoabietinol. This has the formula $C_{40}H_{60}O_2$ and is present to the extent of about $6\%$. Traces of *dextro*-borneol were obtained. From the alkaline solution another monobasic acid, succinosilvinic acid, was obtained on acidification. This acid has the formula $C_{24}H_{36}O_2$, melts at $104°$, and is present to the extent of about $4\%$. The matter insoluble in alcohol, on hydrolysis with alkali yields succinic acid ($2\%$) and succinoresinol, $C_{12}H_{20}O$ ($3\%$). The traces of sulphur found in succinite are in some way associated with the succinoresinol. The remainder of the matter insoluble in alcohol is an indifferent substance, succinoresene, which forms $65\%$ of both varieties of amber. It has the composition $C_{22}H_{36}O_2$ and melts at $324°$. By distillation *in vacuo* this substance yields a mixture of terpenes and phenols.

Small quantities of sulphur are present in most varieties of amber. Gedanite is said to be free from this element, although its main constituents are similar to those of ordinary succinite. Glessite differs from succinite in the absence of the bornyl radical, which is replaced by the carvyl group. Free succinic acid is stated by P. Dahms to be present in amber in proportions ranging from 3 to $8\%$, but its presence is denied by other observers.

**Uses.**—This resin is at present largely employed for the manufacture of ornamental articles. It is also used in the artificial silk industry to increase the elasticity of the finished article. Formerly the darker ambers were used in the varnish industry, but this resin is now very expensive, and in addition there are difficulties in the manufacture which make the resulting varnish too dark for ordinary use. The general public still considers amber varnish as the best commercial variety, but in trade circles it is known that only very small quantities of the varnish sold under this name really contain amber.

**Adulterants.**—Soft copals, specially prepared rosin, and the amber-coloured fluorides are frequently used as adulterants, and it is imitated artificially by coloured glass and celluloid. The imitation

amber previously mentioned is also sold in place of the genuine article.

**General Properties.**—Amber varies in colour, transparency, and translucency. Often the same sample shows marked variation in this respect. The colour varies from pale yellow, through shades of dark yellow and brown, to black. Some specimens are transparent, others are opaque, while intermediate varieties—the cloudy ambers —are also found. Amber is a hard, brittle substance which breaks with a conchoidal fracture. It is the hardest known resin, and in the terms of Mohr's scale has a hardness from 2 to 2.25. The fused resin gives a slightly lower figure. When rubbed, it polishes readily, and at the same time becomes negatively electrified, emitting an odour which is characteristic for the resin.

**Specific Gravity.**—1.08 may be taken as an average figure, but the gravities of different samples vary from 1.050 to 1.096.

**Melting-point.**—When heated to 287° amber melts with decomposition, and when the heating is continued water, succinic acid, small amounts of volatile fatty acids, and a camphor-like substance together with oil of amber are given off, leaving a residue which is completely soluble in turpentine and drying oils.

**Solubility.**—Amber is soluble only to a small extent in most of the usual organic solvents. Dichlorhydrin is one of its best solvents. In alcohol, methyl alcohol, petroleum and acetone, amber is practically insoluble either before or after melting, and in acetic acid, ether, amyl alcohol, benzene, and chloroform before melting, when it is partially soluble in carbon disulphide and oil of turpentine. Amber after melting is partially soluble in ether, amyl alcohol, acetic acid, and chloroform, and almost entirely soluble in benzene, carbon disulphide, and oil of turpentine.

**Analytical Data.**—The following analytical characters of genuine amber have been recorded:

|  | R. Williams | A. Kremel |
|---|---|---|
| Water, %..................................... | 1.05 | ............... |
| Ash, %....................................... | 0.28 | ............... |
| Acid value.................................. | 15.4 | 33.4 to 34.4 |
| Ester value................................. | 71.4 | 74.5 to 91.1 |

A sample of natural amber having a total saponification value of 144.8, was found by von Schmidt and Erban to give the figure 36 after melting, thus showing that this process resulted in the destruction of the greater part of the esters.

**Detection of Adulterants.**—1. Imitation amber. Genuine amber is double refracting, and when viewed by polarised light (with crossed Nicol prisms) it shows only very faint colours, whereas the want of homogeneity of the pressed article causes it to exhibit brilliant tints.

2. Soft copals. (*a*) Cajeput oil dissolves the copals, whereas amber is insoluble in this medium. (*b*) Amber when held in a Bunsen flame burns without melting. (*c*) When warmed with potassium hydroxide solution, copals give off the characteristic odour of copaiba balsam. (*d*) Rossler states that amber when heated in a hard-glass tube evolves sulphurous fumes which blacken lead acetate paper. This is probably only true for succinite. Copals from all sources give negative results when subjected to this test.

3. Hard copals. Amber can be differentiated from the hard copals by testing the hardness. Livache gives the following method: Take a crystal of rock salt and obtain a polished face by cleavage. Examine the suspected samples by driving a sharp corner of each across the crystal of rock salt, then examine the latter under a magnifying glass. Amber leaves a scratch on the surface of the crystal, but the hard copals are too soft to effect this result.

4. Colophony. (*a*) The presence of colophony considerably increases the acid value of the sample. (*b*) Solubility in alcohol. (*c*) When boiled in water colophony softens. (*d*) Pure amber when spotted with alcohol is unaffected, but a dull spot remains on samples which have been adulterated with colophony.

5. Fluorides, hardened rosin, etc. Attention would be called to these adulterants by the high ash value. The presence of a large percentage of alkaline earth oxides would lead the analyst to suspect hardened rosin as the impurity.

6. Celluloid. Rubbing develops an odour of camphor. It is not electrified appreciably on rubbing. Saponification with alcoholic potassium hydroxide separates the $NO_3$ radical and cellulose.

**Oil of amber** (*Oleum succini*), obtained by destructive distillation of amber, has a limited use in medicine. Authentic samples of amber oil examined by E. J. Parry had a sp. gr. of about 0.950 and

an optical rotation of about $+15°$.   According to Schimmel & Co. (*Semi-annual Report*, April, 1903), the pure oil differs markedly from the commercial article, the optical rotation of the former ranging from $+22.5°$ to $+26°$, and that of the commercial oils from $-2°$ to $+13°$.   There is no doubt that commercial oil of amber is almost entirely distilled from cheap resins other than amber.

## COLOPHONY.   COMMON ROSIN

Common rosin, or colophony, is the fixed residue obtained by the distillation of the turpentine or oleo-resin obtained from various species of pine, but chiefly from *Pinus australis, P. tæda, P. pinaster,* and *P. laricio.*[1]

**Commercial Varieties.**—French and American rosins are the two chief commercial varieties.   The former comes on to the market under the name of galipot, while the various grades of American rosin are designated by letters.   For instance grade A is almost black, other letters denote increasing paleness until W. G. is the so-called "water glass" and W. W. "water white" rosin.

**Chemical Composition.**—Colophony consists chiefly of a mixture of free acids together with small quantities of isomeric or polymeric inert substances and traces of mineral constituents and bitter principles.   The unsaponifiable substances are probably composed of hydrocarbons, similar to those contained in rosin oil, produced by the action of heat on the colophony during the process of manufacture.   The chemistry of colophony has been the subject of various researches with curiously conflicting results.   According to Maly, the principal constituent of colophony is abietic anhydride.   Mach obtained abietic acid from colophony by a preliminary treatment with 70% alcohol, and crystallisation of the insoluble portion from 90% alcohol.   After 30 crystallisations a pure white substance was obtained which began to soften at 148° and melted when slowly heated at 153° to 154°.   As the result of combustion experiments supported by cryoscopic and ebullioscopic determinations, he assigns a formula, $C_{19}H_{28}O_2$, to the acid and puts forward the view that abietic acid, sylvic acid, and pimaric acid are identical.   Tschirch and Studer (*Arch. Pharm.*, 1903, **241**, 495) accept the above for-

[1] After distillation of the essential oil the melted resin is removed from the stills and run through wire strainers into barrels.   The lightest-coloured rosin is obtained from trees which have been tapped for the first time, and it then constitutes about 80% of the oleo-resin.   In subsequent years the proportion of resin in the crude turpentine gradually increases, and the resin from a given tree also becomes darker year after year.

mula as correct, although their analyses, even taking into consideration the probability of oxidation, do not agree with the suggested formula.

W. Fahrion investigated samples of American rosin; he found it to consist chiefly of an acid which he calls sylvic acid.  This exists in colophony in an amorphous form, which on treatment with dilute alcohol or when acted on in alcoholic solution with hydrochloric acid gas is converted into a crystallisable modification, which melts at a higher temperature, and is reconverted into the amorphous form by prolonged heating; secondary products are also produced.  The m. p. of abietic acid is very variously stated, Mach giving it at 153° to 154°, Dragendorff at 144°, and others again as high as 165°. P. Levy (*Zeit. angew. Chem.*, 1905, **18**, 1739) has obtained from colophony, by vacuum distillation and crystallisation of the product many times from methyl alcohol, pure abietic acid with a m. p. of 182°.  The elementary analysis and molecular weight determinations together with an examination of the derivatives has proved the correctness of the formula proposed by Bischoff and Nastvogel and accepted by Fahrion.[1]  When its alcoholic solution is slowly evaporated abietic acid is deposited in crystalline laminæ.  Prolonged heating is stated to convert abietic acid into its anhydride.

Abietic acid is quite insoluble in water, but dissolves readily in strong alcohol, ether, chloroform, benzene, carbon disulphide, and glacial acetic acid.  According to Mach, abietic acid dissolves in strong sulphuric acid with red colour.

According to W. Fahrion, abietic acid oxidises spontaneously with formation of *peroxides* containing $C_{20}H_{30}O_4$ and $C_{20}H_{30}O_6$. These substances are insoluble in petroleum spirit, but undergo intramolecular change with formation of *dihydroxy-abietic* and

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[1] W. Fahrion adopts the formula $C_{20}H_{30}O_2$ for abietic (sylvic) acid, and confirms the following constitutional formula proposed by Bischoff and Nastvogel:

$$CH:C(CO_2H).CH.CH.CMe = CH$$
$$CH_2.CHPr - CH.CH.CHPr.CH_2$$

(Pr = Propyl).
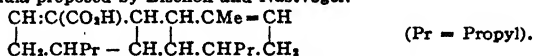
Fahrion has shown that abietic acid is very liable to spontaneous oxidation, and this is the cause of the low values for carbon and hydrogen obtained by certain other workers on this substance.

While agreeing in ascribing to pimaric acid the formula $C_{20}H_{30}O_2$, observers differ greatly as to its character.  According to A. Vesterberg (*Ber.*, 1885, **18**, 3331; 1886, **19**, 2167) 1887, **20**, 3248), two varieties of pimaric acid exist.  *Dextropimaric acid* has a specific rotation in alcoholic solution of $+72.5°$, melts at 210° to 211°, and distils in a vacuum almost unchanged and without formation of sylvic acid.  Ammonium dextropimarate is said to separate in fine needles when an ethereal solution of the acid is agitated with ammonia. *Lævopimaric acid* is very strongly lævorotatory ($[\alpha]_D = -272°$), and melts between 140° and 150°.  S. Haller (*Ber.*, 1885, **18**, 2165) describes pimaric acid as optically inactive and melting at 149°.  Pimaric acid is said to differ from abietic acid in having a bitter taste.

*tetrahydroxy-abietic acids*, $C_{20}H_{29}(OH)O_3$ and $C_{20}H_{28}(OH)_2O_4$, which are soluble in petroleum spirit. The latter acid is also produced by the oxidation of abietic acid by permanganate in alkaline solution. Other indefinite products are also formed by the oxidation of abietic acid and occur in colophony.[1]

Abietic acid is frequently described as dibasic, but the presence of only one carboxyl group in the molecule and the proportion of alkali required for its neutralisation conclusively negative this view. Abietic acid forms a series of salts, some of which are crystallisable. The abietates of the alkali metals are readily soluble in water, alcohol, and ether, and are possessed of marked detergent properties. Hence the employment of rosin in soap-making. An acid potassium abietate, obtained by Mach by neutralising an alcoholic solution of abietic acid with alcoholic potash, or boiling it with potassium carbonate, forms bundles of silky needles melting at 183°. The normal potassium salt also crystallises in silky needles, while the barium salt is described as a white, amorphous compound, which becomes yellow on exposure to air.

According to Perrenoud, the ammonium salt of abietic acid from colophony is gelatinous, whereas the acid ammonium salt of pimaric acid crystallises in handsome needles.

Aschan (*Ber.*, 1921, **54**, 867) has isolated a new series of acids from both American and Finnish colophony. The acids have the general formula $C_nH_{2n-10}O_4$ and have been provisionally named from the number of carbon atoms present. Thus $C_{16}H_{22}O_4$ is hexadecacolophenic acid. They are monobasic, in spite of the presence of four oxygen atoms. One hydroxyl group is also present.

The acids are colourless or pale yellow, but form darker salts with alkalies. The sodium salts of these colophenic acids are freely soluble in water, and the solutions are not affected by carbon dioxide. The barium, calcium, silver, and copper salts are fairly soluble in water. The isolation of these acids is effected in the following manner. The colophony is dissolved in hot aqueous solution of sodium carbonate, and the solution when cold is treated with carbon dioxide until the precipitation of acid resinates is com-

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[1] F. Jean (*Chem. News*, 1872, **26**, 207) has described three acid resins as occurring in colophony. Resin A, probably identical with abietic acid, is insoluble in water, but soluble in alcohol, ether, and oil of turpentine. Resin B is insoluble in the last solvent, and is also distinguished from A by yielding a sodium salt insoluble in sodium hydroxide solution of 1.116 sp. gr. Resin C is soluble in water, and its aqueous solution is precipitated by silver and cupric salts. Tschirch and Studer claim to have isolated 3 isomeric abietic acids from American colophony. Two of the acids form insoluble lead salts (*Arch. der Pharm.*, 1903, **241**, 495).

plete. The filtrate is then acidified and the crude acids resulting are separated, dissolved in benzene and precipitated from this solvent by the addition of petroleum spirit, in which the acids are insoluble. The following colophenic acids have been described. Hexadecacolophenic acid, $C_{16}H_{22}O_4$, forms large fellow granules melting at 96–105°, or a practically colourless powder, melting at 86–98°. Its specific rotation is about $+21°$ or $+22°$. It appears to be prepared artificially by the action of hydrogen peroxide on a slightly alkaline solution of pinabietic acid.

Heptadecacolophenic acid, $C_{17}H_{24}O_4$, melting at 100–105°, was obtained from Finnish colophony.

Octadecacolophenic acid was isolated from American colophony.

Eicosocolophenic acid was obtained from two dark brown specimens of American colophony. This acid softens at 80–90° and is completely melted below 110°

**Uses.**—Colophony is employed very largely in the manufacture of soap, for the preparation of varnishes and resinate driers in the varnish industry, to a certain extent in pharmacy, especially in veterinary practice, and the soluble salts are now used in the paper industry for sizing paper. Large quantities of rosin are also employed in the manufacture of rosin oil.

**Adulterants.**—Colophony is such a cheap material that it is very rarely adulterated, but it is a favorite adulterant of the more expensive resins, such as shellac, dammar, dragon's blood, guaiacum, storax, benzoin, etc.

**General Properties.**—Colophony, or rosin, is a soft transparent or translucent resin of a faint terebinthinate odour which is more noticeable when the resin is held in the hand. It is nearly tasteless, but some varieties possess a nauseous and highly characteristic after-taste. Colophony is very brittle, and shows a shallow conchoidal fracture when broken. It varies in colour from a very pale amber to a very dark reddish-brown. The darkest kind is known commercially as black rosin. Powdered rosin varies in colour from white to pale yellow.

**Specific Gravity.**—The sp. gr. of this resin usually lies between 1.045 and 1.085 Dieterich gives 1.045 to 1.086 as the limit figures for commercial good samples. This constant may be conveniently ascertained by immersing small pieces of the resin free from air bubbles and mechanical impurities in brine solutions of varying

densities and estimating the gravity of the solution in which they remain suspended.

**Melting-point.**—Colophony has no sharply defined m. p. It softens at a temperature of 70° to 80°, becomes semi-fluid in boiling water, and melts completely at a somewhat higher temperature. The final point of fusion varies with different samples, but 135° should not be exceeded. When heated in the air colophony ignites and burns with a yellow and very smoky flame, leaving a trifling quantity of ash. When the flame is blown out a highly characteristic odour is noticeable. On distillation colophony undergoes a complex decomposition with the production of two important products, rosin spirit and rosin oil, both of which are described elsewhere.

**Solubility.**—Colophony is quite insoluble in water, although it contains small proportions of soluble substances. At 60° it dissolves slowly in an equal weight of alcohol or glacial acetic acid, and is also readily dissolved by methyl and amyl alcohol, acetone, ether, chloroform, carbon disulphide and the fixed and volatile oils. Petroleum spirit does not dissolve colophony completely. Dieterich put forward the suggestion that not more than 7% of a good quality rosin should be insoluble in this medium, but experience has proved that the insoluble portion may vary from 1 to 20% in samples which are suitable for certain commerial purposes.

According to W. Fahrion, colophony for use in varnish manufacture should be light in colour and have a high acid value approaching to that of sylvic acid, 185.4. The quantities of material insoluble in petroleum spirit and the amount of unsaponifiable matter should be small.

**Analytical Data.**[1]—(a) Ash, extremely small. (b) Acid value. The acid value of colophony normally ranges between 150 and 175. This represents a proportion of resin acids in terms of $C_{20}H_{30}O_2$ ranging from 83.4 to 93.8%. Dieterich suggests the following method for the determination of its value:

About 1 grm. of the finely powdered material is suffused with 25 c.c. of alcoholic potassium hydroxide and left covered until the whole has dissolved. The excess of alkali is then titrated back with

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[1] K. Dieterich has suggested that rosin should pass the following standard tests: It should be as light coloured as possible, and when boiled with water the extract should, when tested with ferric chloride solution, give a minimum colour reaction. In alcohol, ethereal oils, acetone, ether, chloroform, methyl alcohol, amyl alcohol, acetic ether, benzol, oil of turpentine, and carbon disulphide it should be completely soluble, and partly soluble in benzin and petroleum spirit.

The acid value when indirectly determined should only vary between 145 and 185. The quantity of ash should be small.

sulphuric acid. The number of c.c. of alcoholic potassium hydroxide required multiplied by 28.08 gives the acid value (indirect). It is extremely doubtful whether the above method offers any advantages, except that it determines both the actual free acids and lactones. The continued action of the alkali may affect the substances other than true acids in the resin and falsify the results. Direct titration in alcoholic solution with alcoholic potassium hydroxide can be strongly recommended to give constant results. (*c*) Ester value. In addition to the free acid value obtained by direct titration of the resin in alcoholic solution with alkali hydroxides and phenolphthalein, colophony neutralises a small additional quantity of alkali on complete saponification. This additional neutralising power was at first thought to be due to the presence of resin esters, but R. Heinriques (*Chem. Rev. Fett. Harz Ind.*, 1899, **6,** 111) claims to have proved the absence of these. Probably the hydrolysis of abietic anhydride or lactone acids causes the extra quantity of alkali to be neutralised. This value varies considerably in different samples of rosin and can scarcely be used as a means of identification.

The following table shows the acid and saponification values recorded for various samples of commercial rosin. The ester values are the differences between the two former figures.

| Kind of rosin | Acid value | Ester value | Saponification value | Observer | Reference |
|---|---|---|---|---|---|
| American (6 samples).... | 154.1 to 164.6 | 15.7 to 30.0 | 174.7 to 194.3 | J. Lewkowitsch | *J. Soc. Chem. Ind.*, 1893, **12,** 505. |
| Austrian................ | 146.0 | 21.1 | 167.1 | v. Schmidt & Erban | *J. Soc. Chem. Ind.*, 1889, **8,** 308. |
| Typical (6 samples)...... | 154.0 to 162.0 | 14.4 to 19.8 | 174.3 to 177.6 | Smetham & Dodd | *J. Soc. Chem. Ind.*, 1900, **19,** 102. |
| White.................. | 172 | 7.0 | 179 | H. Amsel | *Zeits. ang. Chem.*, 1896, **9,** 429. |
| Yellow; new............. | 162 | 7.0 | 169 | H. Amsel | *Ibid.* |
| Yellow; old............. | 167 | 8.0 | 175 | H. Amsel | *Ibid.* |
| Very pale.............. | 155 | 12 | 167 | A. H. Allen | Unpublished note. |

In addition to the above data, A. Kremel (*Pharm. Jour.*, 1887, [3], **17,** 547) found acid values varying from 151.1 in dark Austrian colophony to 173.6 in an American specimen. Beckurts and Brüche have recorded 180, 181, and 185 as the acid values of samples of white, brown, and yellow rosin, respectively, and give identical figures for the saponification values of the same samples, a result which is improb-

able.   In red rosin they found acid values ranging from 173 to 186, with saponification values from 179 to 193.

Two samples of American colophony analysed by A. H. Allen and S. O. Richmond gave the following results:

|  | Pale | Brown |
|---|---|---|
| Sp. gr. | 1.069 | 1.081 |
| Acid value (by titration with aqueous alkali, A) | 157.9 | 172.4 |
| Acid value (by titration with alcoholic alkali, $a$) | 154.0 | 168.4 |
| Total saponification value (B) | 169.4 | 176.2 |
| Ester value (B—A) | 11.5 | 3.8 |
| Ester value (B—$a$) | 15.4 | 7.8 |
| Unsaponifiable matter, % | 9.25 } 9.93 | 4.28 |

It will be observed that the figures obtained by dissolving the sample in strong alcohol, and titrating the solution with alcoholic alkali hydroxide, are somewhat lower than those obtained when seminormal aqueous sodium hydroxide was employed for the titration, but the differences are not great.   As the total saponification value was determined by titrating back the alcoholic alkaline liquid with aqueous hydrochloric acid, the figures for free acid obtained by titration with aqueous alkali have been used in calculating the following composition of the samples from the data recorded above:

|  | Pale | Brown |
|---|---|---|
| Abietic acid ($C_{20}H_{30}O_2$) | 85.16% | 92.96% |
| Abietic anhydride ($C_{40}H_{58}O_3$) | 6.04% | 1.99% |
| Hydrocarbons (unsaponifiable matter) | 9.25% | 4.28% |
|  | 100.45 | 99.23 |

These results indicate that the samples examined consisted chiefly of abietic acid, and did not contain any large proportion of abietic anhydride or lactone acids.   The unsaponifiable matter was of a very pale straw-yellow colour.   That from the pale rosin was soft and "tacky," but that from the brown sample was somewhat harder.

The sample of pale rosin described above was also examined by Tschirch's process with the following results:

|  |  | %. | Combining weight |
|---|---|---|---|
| Resin acids.............. | Soluble in 1 % ammonium carbonate solution.......................... | 2.62 | 326.6 |
| | Soluble in 1 % sodium carbonate solution............................. | 88.62 | 343.9 |
| | Soluble in 1 % sodium hydroxide solution........................... | 0.64 | |
| Unsaponifiable matter...... | Volatile with steam (terpenes)....... | 1.00 | |
| | Not volatile with steam............. | 6.05 } | 7.05 |
| | | 98.93 | |

The original sample of pale rosin, and the separated resin acids and unsaponifiable matter, all gave a fine purple coloration, fading slowly to brown, when they were dissolved in a little acetic anhydride, and a drop of sulphuric acid (sp. gr. 1.53) added. When dissolved in acetic anhydride and a drop of stannic tetrabromide added, a purple coloration was produced in each case, the colour fading slowly to dark brown.

**Unsaponifiable Matter.**—Holde und Marcusson (*Mittheil. Königl. tech. Versuchsanstalt.*, 1902, 40) state the average amount of unsaponifiable matter in colophony as 8%. The highest recorded amount is 15.94%, which was found by Lewkowitsch in a sample having an acid value of 146.5 and a saponification value of 153. Ulzer gives 4.76 and 5.9% as the quantity of unsaponifiable matter in two samples of Austrian rosin.

**Acetyl Value.**—K. Dieterich has obtained the following results for this value:

By titration of the acetylated resin with alkali....... 155.8
By back titration, after saponification (ester value).... 92.1 to 95.4
Difference ( = saponification value of acetylated resin).. 251.2 to 274

Kitt has found the *carboxyl value* of colophony to be insignificant (about 0.5%).

Gregor and Bamberger obtained negative results for the *methoxyl value* of colophony.

The *iodine value* of colophony has been determined by E. J. Parry (*Chemist and Druggist*, Jan. 31, 1903) and found to average 125 of the Hübl method. By the Wijs method it is about 228. This will be referred to under shellac, where the estimation of the iodine value is the standard method of analysis:

**Detection and Estimation of Colophony.**—When unmixed with interfering substances colophony is readily recognised by its physical characters.

A valuable reaction for colophony, originally suggested by Lieber-mann, but modified by Storch and Morawski, consists in treating the substance with acetic anhydride, cooling the liquid, and separating the acetic anhydride with a pipette or other suitable arrangement. Sulphuric acid of 1.53 sp. gr. is then allowed to flow gently into the tube containing the acetic anhydride, when a reddish-violet colour will be immediately produced at the junction of the two liquids if colophony be present. The colour soon changes to reddish-brown. According to Allen, a preferable plan is to place from 10 to 20 drops of the acetic anhydride solution in a flat porcelain dish (or the inverted cover of a porcelain crucible), and cautiously add a drop or two of sulphuric acid of the above strength. The coloration is seen more readily against a white background than when a test-tube is used.

Fatty acids do not produce a similar colour, but cholesterol and some other substances simulate the reaction of colophony. Choles-terol may be separated by shaking the substance with aqueous soda and ether, separating the alkaline liquid, and acidifying it with sulphuric acid. The precipitate of resin acids should be separated and dissolved in acetic anhydride.

P. Foerster (*Ann. Chim. Anal. Appl.*, 1909, 14, 14) has suggested the following modification of Halphen's test for the detection of rosin oil in mineral oils, which enables traces of colophony to be detected in other substances. Two solutions are necessary: (*a*) 1 part by volume of phenol in 2 parts of carbon tetrachloride. (*b*) A solution of 1 part of bromine in 2 parts of carbon tetrachloride. When a small amount of colophony is dissolved in 2 c.c. of solution *a*, and the basin is brought close to solution *b*, the bromine vapours given off by the latter produce at the point of contact a blue coloration, which changes to violet under the continued action of the bromine. When rosin oil is present a violet colour is produced at once. It is usually necessary before applying the test to isolate the colophony.

A fairly approximate estimation of rosin, when in admixture with neutral fatty oils, may be effected by dissolving the sample in a mixture of alcohol and ether, and titrating with standard sodium hydroxide solution. Taking 165 as the average acid value of colophony, each c.c. of $N/10$ alkali neutralised by the sample repre-sents 0.0340 grm. of colophony present. As the neutralising power of rosin varies materially, the result obtained as above can only

claim approximate accuracy.   It is, of course, further affected by
free fatty acids, which, if present in quantity, will entirely vitiate
the estimation.   The process is, however, convenient and of consid-
erable practical utility.   Thus, it has been employed for approxi-
mately ascertaining the proportion of rosin in a mixture of that
substance with linseed oil used as *bird-lime.*

For the estimation of colophony in cerasin and paraffin, the sample
should be boiled several times with 70% alcohol.   The alcoholic
liquid is filtered when quite cold, and the filtrate distilled.   The resi-
due of resin is dried at 110° to 115° and weighed.   If fatty acids are
present, they will be extracted with the resin and must be subse-
quently separated.

The separation of fatty and resin acids is necessary for the esti-
mation of colophony in soap.   It presents considerable difficulties,
as the fatty acids vary somewhat in chemical and physical characters
according to their source, and colophony is itself of complex and
variable composition.   The processes practically available are those
of Barfoed, Gladding, Twitchell and Wolf, or modifications or com-
binations of these.   These methods are fully described in Vol. 2.
Twitchell's and Wolf's are by far the most satisfactory process, and
is sufficiently accurate for many purposes.   When, however, it is
desired to estimate the proportion of colophony in soap with the
greatest attainable accuracy, a combination of Twitchell's and
Gladding's methods, described by Holde and Marcusson (*Mittheil.
Königl. tech. Versuchsanstalt.*, 1902, 40), may be advantageously
employed.   In this process special attention is paid to the washing
of the immiscible solvents employed, the resin acids soluble in water
are recovered, and the unsaponifiable matter natural to the colophony
is estimated or allowed for.   The process is as follows:

A quantity of the sample representing about 5 grm. of fatty and
resin acids is boiled with 50 c.c. of alcoholic potassium hydroxide
for half an hour under a reflux condenser.   The alcoholic solution is
then evaporated, the residue dissolved in water, and any unsaponifi-
able matter removed by agitation with ether.   The aqueous layer is
separated and acidified with hydrochloric acid.   Soaps containing no
unsaponified fat or unsaponifiable matter may be directly dissolved
in water and decomposed with acid.   The separated acids are
removed by shaking with ether; the aqueous acid solution is neutra-
lised, evaporated to about 25 c.c., reacidified, and shaken out with

ether.   After distilling off the ether from the united ethereal extracts
the residue of resin and fatty acids is dissolved in 50 c.c. of absolute
alcohol, and the fatty acids converted into esters by passing a moder-
ately rapid current of dry hydrogen chloride gas through the solution
cooled by ice-water to a temperature not above 10°.   When the
operation is complete (which is usually the case in from 1 to 2 hours),
the liquid is allowed to stand for half an hour at the ordinary tem-
perature.   It is then diluted with five times its volume of water,
and boiled under a reflux condenser for half an hour.   The cooled
solution is agitated with several successive quantities of ether until
the extracts are colourless.   The aqueous liquid is neutralised,
evaporated to 50 c.c., acidified, and repeatedly extracted with
small quantities of ether to recover the water-soluble constituents of
colophony.   The mixed ethereal solutions are shaken out with
about 50 c.c. of a solution containing 10 grm. of potassium hydroxide,
10 grm. of alcohol, and 100 c.c. of water, when a brown layer usually
separates out between the ether and the alkaline solution, and is
drawn off with the latter.   This layer contains a considerable
portion of the resin soap, which is only slightly soluble in the potash
solution.   The ether is shaken with water to remove soluble resin
soaps; then with 2 successive quantities (10 c.c.) of the potash
solution; and finally with water until the washings are colourless.[1]
The alkaline liquid is now acidified and agitated with ether until
completely extracted.   The acid solution is neutralised, evaporated
in a small bulk, reacidified, and again shaken out with ether.   The
total ether extracts are washed with 20 c.c. of water, and the ether
distilled off.   The residue of resin acids so obtained—still contami-
nated with unchanged fatty acids—is treated with several small
successive additions of absolute alcohol to remove the last traces
of water, and weighed.   The fatty acids still remaining in the resin
acids are removed by Gladding's process.   From 0.4 to 0.6 grm. of
the resin acids, obtained as above, should be placed in a 100 c.c.
stoppered and graduated cylinder and dissolved in 20 c.c. of 95%
alcohol.[2]   A drop of phenolphthaleïn solution is added to the alco-
holic solution, and then concentrated sodium hydroxide solution
(1 of NaOH to 2 of water) until the reaction is just alkaline.   The

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[1] In the presence of fish-oil acids or much colophony the washing with water must be
very thorough.
[2] If only a small amount of resin acid is obtained, the prescribed proportions of the ether-
alcohol mixture must be correspondingly altered, while in the case of a large yield of acids,
it is advisable to dissolve the whole in so much 95% alcohol that 20 c.c. of the solution
shall contain 0.5 grm. of resin acids.

loosely-stoppered cylinder and its contents are heated for a short time in the water-bath, then cooled, and ether added up to the 100 c.c. mark. 1 grm. of dry powdered silver nitrate is added, and the contents of the cylinder are shaken for 15 minutes to convert the fatty and resin acids into silver salts.

When the insoluble salts have completely settled (preferably after standing overnight), 70 c.c. of the solution should be pipetted into a second 100 c.c. cylinder and shaken with 20 c.c. of dilute hydrochloric acid (1:2). The ethereal layer is drawn off, and the aqueous liquid twice shaken with ether. The united ether extracts are washed with water, filtered, and the ether distilled off. The residue, amounting to about 10 c.c., is evaporated, dried for a short time at 110° to 115°, and weighed. The weight of the resin acids so found is calculated back into the first weight (impure acids) obtained, and then on the original substance taken. The percentage found is corrected by the subtraction of 0.4%, this allowance being made for a small amount of unesterified fatty acid which is always present. As colophony contains an average of 8% of unsaponifiable matter, a second correction is necessary, the true percentage of colophony of the substance under examination being found by the following equation, in which the corrections are combined:

$$100 \frac{\text{(Percentage of resin acids found—0.4)}}{92} = \% \text{ of colophony}$$

## COLOPHONATES. RESINATES

Colophony dissolves in solutions of alkali hydroxides, and of alkali metal carbonates, with formation of so-called resin soaps consisting of impure abietates.

**Commercial Varieties.**—The lead, manganese, calcium, zinc, potassium, and sodium salts are now articles of commerce. Potassium and sodium resinates have marked detergent properties, and are extensively employed in the manufacture of the commoner kinds of soap. Resin soaps have a remarkable emulsifying power (see H. Collier, *Pharm. J.*, 1889 [3], **20, 751**), and this property finds an extensive application in the manufacture of sheep dips, kerosene emulsions for spraying, etc., and phenolic disinfecting fluids. The metallic resinate of manganese and lead are often added to boiled linseed oil, and are now employed in the manufacture of varnishes.

Colophony has always been used in the varnish industry, but formerly it was only employed for special purposes. This soft gum could only be combined with a small quantity of oil, and the resulting varnish rubbed up as a white powder. Zimmermann first observed that greater hardness could be obtained by the neutralisation, or partial neutralisation, of the resin acid by the addition of an oxide of the alkaline earths. This method has been further investigated, and at the present time large quantities of these salts are used commercially.

**Resins esters** are now produced from colophony by condensation with higher and lower alcohols, especially glycerin and phenols. These compounds are of some importance because they are found in commerce under fancy names, as gum or shellac substitutes, or sold as ester gums.

### Identification and Valuation.

1. **Resin Soaps.**—Sodium resinate is a deliquescent brown powder which is very soluble in water. The taste is resinous and very acrid. Resin soaps differ from those of the fatty acids in not being readily precipitated from their aqueous solutions by the addition of brine. Resin soaps are also differentiated by their solubility in ether or ether-alcohol, a fact utilised by Barfoed for the separation of fatty from resin acids. Jean and Remont have proposed to utilise the solubility of barium colophonate in alcohol to effect the same separation, while Gladding has described a method of separating fatty from resin acids based on the ready solubility of silver colophonate in ether, and almost complete insolubility of silver oleate, etc., in the same menstruum, even in presence of some alcohol.

2. **Driers (Lead and Manganese Resinates).**—These preparations of colophony, commercially known as resinate driers, are of very variable composition. They are either prepared by melting rosin with the oxide of the metals or by the addition of a soluble metallic salt to the aqueous solution of a resin soap. The commercial products are mostly prepared by the former method, consequently they usually contain a large proportion of free resin acid. The fused resinates are brown to dark brown in colour with the appearance of dark rosin. Commercial precipitated lead resinate is light brown, and the corresponding manganese salt has a pinkish hue. Both manganese and lead resinates are used, but for general purposes a mixed resinate containing lead and manganese in the proportion of 5 to 1

is the most suitable. This product contains 8 to 9% of soluble lead and 1.5 to 2% of soluble manganese.

Meister (*Farbenztg.*, 1907, **51**, 1614) has examined a number of commercial lead and manganese resinates, and obtained the following results:

| Material | Manganese, % | Manganese, resinate, % | Lead, % | Lead resinate, % |
|---|---|---|---|---|
| Fused manganese resinate............ | 2.5–3 | 45–55 | ....... | ........... |
| Fused lead manganese resinate........ | 1.5 | 27 | 9–10 | 40 |
| Precipitated manganese resinate....... | 5.7–6.5 | 80 | ....... | ........... |
| Precipitated lead resinate............. | ........... | ........... | 20–23 | 80 |

These resinate driers are now widely used. The general physical properties, that is, colour, hardness, etc., are of very slight importance for their valuation. The total quantity of mineral matter present must not be taken as an approximate measure of value as suggested by Amsel (*Zeit. angew. Chem.*, 1896, **9**, 429).

The drier must be completely soluble in linseed oil at 120°. Any oxide which remains suspended is not only valueless as a drier, because it cannot act at the low temperature at which the oil is treated, but it forms a foot or turbidity which directly impairs the quality of the oil. Although the proportion of insoluble oxide should be as small as possible, the proportion of uncombined acids should also be small, since the presence of these acids decreases the percentage of active metal. Although values obtained by analysis are helpful in judging the quality of a drier, there are other important considerations. Driers of the same apparent chemical composition behave so differently when applied to their special use, that practical tests are extremely important. Numbers of experiments have proved that one and the same resinate from different sources, *e. g.*, precipitated manganese resinate, gives varying results. Some cause oil to fatten, that is to become thick, others bleach the oil; some give foots, others give minimal quantities of the same. In view of these difficulties Andes has suggested the adoption of the following methods for obtaining true information regarding the value of the drier under examination.

For these tests it is necessary to have well-matured linseed oil which when heated to 270° to 300° shows no signs of yielding a deposit. If this is not available, ordinary commercial linseed oil

should be first heated to this temperature, and then allowed to stand several days before use. The test can be made in two ways: (*a*) By solution of the drier in linseed oil, with and without heat. (*b*) By solution in turpentine and mixing the solution so obtained with linseed oil.

(*a*) Precipitated resinates dissolve in linseed oil at ordinary temperatures. The oil is shaken occasionally with 1.5% of the drier for 24 hours and then allowed to stand. Fused resinates are not soluble in the cold, so they must be heated with the oil to a temperature of 120°.

(*b*) Dissolve in turpentine in the proportion of 1 part to 4 parts of turps with application of heat. Add from 5 to 10% of this solution to linseed oil, shake together, and allow to stand.

The solutions obtained in this way are filtered into tall square bottles and allowed to stand at least 4 days. The colour, transparency, and the amount of precipitate is then observed. That drier is the most satisfactory which colours least, remains clear, does not thicken, and gives the smallest amount of precipitate. The drying test is also of great importance. The oil should be spread on a glass plate about 5 × 5 in. square and stood on a rack at an angle of 75° to 80°. Under these conditions the oil should dry to an elastic skin in 5 or 6 hours.

**Analysis of Driers.**[1]—The resinates contain soluble and insoluble oxides of the metals. The total quantity of metallic oxide present can be found by an estimation of the constituents in the ash, while

[1] Max Weger (*Chem. Rev. Fett Hars-Ind.*, 1897, **4**, 303) has written as follows respecting the valuation of resinate driers. The most active, and *a priori* the most useful drier is that in which the highest possible amount of soluble lead or manganese, respectively, are present, combined with the absence of insoluble oxides. In practice this is not the case. It is often necessary to accept a percentage of free resin acids which offer an important advantage in the processes used by the oil and varnish manufacturer. It is often desired, or for some purposes it is absolutely necessary, that the resinate should be dissolved at a low temperature, and the presence of the free resin has an important influence on the temperature at which the drier is taken up. A melted resinate containing 5% of soluble manganese would theoretically be superior to a similar resinate containing only 4%. Under certain conditions this might be the case; on the other hand, a resinate containing 4% of soluble manganese might be applicable, yet a resinate containing only 3% would suit the conditions much better. A drier suitable for the preparation of a liquid terebine might be totally unsuitable for direct use in varnishes, and *vice versa*. The special application for which the drier is intended is the important consideration. That product is not the most suitable which contains the theoretical quantity of lead or manganese, respectively, but that article which suits the total requirements of the manufacturer, relating to drying power, colour, temperature of solution, behaviour toward pigments, etc. It would be absolute foolishness, and show a total ignorance of practical conditions, to give an opinion on a drier based on analytical results, without due consideration of the special purpose for which the drier is intended. Under such conditions it would be easily possible to describe the most suitable product as unsatisfactory and *vice versa*. Even when the exact practical requirements are known, long practical experience is essential, to enable a chemist with some surety to base his opinion on an analysis of these products, and even then it would be advisable to confirm the conclusions by practical tests. Practical tests for the valuation of these products, as with most other materials used in the varnish industry, were and remain absolutely the determining factors.

the soluble oxides can be separated from the resinate by treatment with a solvent in which the metallic resinates are soluble. R. Hefelmann (*Chem. Rev. Fett Harz-Ind.*, 1901, **8**, 191) uses the following method: 10 to 15 grm. of the powdered resinate drier is agitated with chloroform, and filtered in to a measuring flask and made up to 250 c.c. 50 c.c. of the extract are then treated in an Erlenmeyer flask with alcoholic hydrogen sulphide. The lead sulphide is well washed, dried, and weighed. The filtrate, if it contains manganese, is evaporated, and the manganese is estimated in the residue.

**Estimation of Free Resin Acid.**—Marcusson and G. Winterfeld (*Chem. Rev. Fett Harz-Ind.*, 1909, **16**, 104); see also Holde (*Mineralöle und Fette*, 1905, 377). The estimation is carried out in the following way: 10 to 20 grm. of the sample are dissolved in 50 c.c. benzene. The solution is filtered, 30 c.c. of hot water coloured with methyl orange are then added, and the whole is titrated with N/2 hydrochloric acid until after warming and shaking the water layer retains a pink colour. The benzene layer is then separated from the water, well washed, mixed with neutral alcohol, and again titrated with a N/10 sodium hydroxide solution in the presence of phenolphthaleïn. From these two titrations the amount of free resin acid present can be calculated.

3. **Hardened Rosin.**—*a. Metallic Resinates.*—These substances are now largely used as constituents of varnishes. They do not soften at such a low temperature as ordinary rosin, and feel less sticky when held in the warm hand. Unlike colophony they are insoluble in alcohol, but dissolve in linseed oil and turpentine, giving more or less quick-drying varnishes. Water decomposes all these compounds, *e. g.*, the barium, calcium, strontium, and zinc salts; consequently, although such varnishes are comparatively suitable for in-door work, when exposed to the weather they are rapidly disintegrated. Varnishes prepared in this manner when mixed with lead or zinc colours do not cause them to thicken, whereas ordinary colophony, particularly with lead, sets hard under these conditions.

(*b*) *Esters of Colophony.*—These compounds are pale in colour easily soluble in oil and turpentine, and possess great brilliancy. In alkaline solutions they are insoluble. It is stated that varnishes prepared from these products dry hard and stand exposure, but, although these statements are made, cheaper and more satisfactory varnishes can be prepared from the commoner varieties of copal.

## DRY DISTILLATION OF COLOPHONY

When rosin is subjected to dry distillation, it undergoes decomposition in a very complex manner.[1]  Besides a variable proportion of unaltered resin, it yields a large number of hydrocarbons, traces of phenolic compounds, and various acids and aldehydes of the fatty series.  Among the last-named have been recognised acetic, propionic,[2] isobutyric, isovaleric, caproic, heptoic, nonoic, and hendecatoic acids; and isobutyric and valeric aldehydes.

The distillation of rosin is practised commercially on an extensive scale for the production of rosin spirit and rosin oil.  The process is conducted in vertical cast-iron stills with hemispherical ends.  The heat is applied directly, and distillation without steam is usually preferred, as in that case the production of spirit is less.  Gas and aqueous liquid are first given off, followed or accompanied by a light, oily liquid, which boils between 80° and 250°, and constitutes the product known as *rosin spirit* (see below).  At about 300°, or somewhat above, *rosin oil* commences to distil, and continues to pass over until the still attains a dull red heat.  Water, containing a little acetic acid, continues to pass over throughout the process, and gases are evolved in considerable quantity.[3]  The residue in the still consists of pitch or coke, according to the stage to which the distillation is pushed.  The yield of rosin oil is generally about 85%, the remaining 15% including from 2.5 to 5% of rosin spirit, a small proportion of water, containing about 1% of acetic acid (*J. Soc. Chem. Ind.*, 1890, **9**, 16), pitch or coke, gases, etc.[4]

### Rosin Spirit

Rosin spirit is the lighter and more volatile oily portion of the product of the dry distillation of rosin.  It is separated from the

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[1] According to Bischoff and Nastvogel (*Ber.*, 1890, **23**, 1919, *J. Soc. Chem. Ind.*, 1890, **9**, 927), if rosin be distilled in a vacuum the products are fewer and more readily separated than when the distillation is conducted at the ordinary atmospheric pressure.  Working on laboratory quantities, by repeated fractionation under 30 mm. pressure, two main fractions were obtained.  The larger of these boiled at that pressure between 248° and 250°, and after a short time solidified to a colourless, brittle, microcrystalline mass, which was insoluble in water, but soluble in alcohol and ether.  It had the composition $C_{40}H_{58}O_3$, and was apparently *abietic anhydride* ("isosylvic anhydride").  It had a specific rotation of +63°, dissolved in a warm solution of potassium hydroxide, and on acidifying the liquid with acetic acid gave an acid having the composition $C_{20}H_{30}O_2$, and melting at 60.5° to 62.5°.  Hence it was an isomer of abietic or sylvic acid.  The other main fraction boiling at 318° to 320° contained $C_{20}H_{32}$, and was a diterpene probably identical with Deville's *colophene*.

[2] Propionic acid was observed by Renard in considerable quantity in the products of the distillation of rosin at a red heat.

[3] The gases contain carbon monoxide, ethylene, butylene, and pentine, and are said to be powerfully anæsthetic.

[4] E. J. Mills has recorded the densities and bromine absorptions of the products distilling at frequent intervals during an entire operation.  The sp. gr. increased from 0.909 to 1.0030 at the end of 20 hours, and then fell to 0.970.  The bromine-absoprtion of the first product was 142 % and gradually fell to 32 % (*J. Soc. Chem. Ind.*, 1885, **4**, 328).

acetous aqueous liquid which distils with it, purified by agitation with sulphuric acid and sodium hydroxide (and sometimes common salt), and is then redistilled.

When thus refined, rosin spirit is a colourless liquid, insoluble in water or alcohol, but miscible in all proportions with ether, petroleum spirit, and oil of turpentine. Rosin spirit presents a close general resemblance to oil of turpentine, the odour, however, is peculiar, and the sp. gr. is more variable, ranging from 0.856 to 0.883. The behaviour of rosin spirit on fractional distillation is also different from that of turpentine oil, and other distinctions exist (see Turpentine Oil).

Rosin spirit has a peculiar and highly complex composition. According to A. Renard (*Ann. Chim. Phys.*, 1884, [6], 1, 223), the hydrocarbons of rosin spirit include pentane, pentene, and their homologues; toluene and its homologues; tetra- and hexa-hydrotoluene, and their homologues; terpenes, etc.[1] Deville found colophene (boiling between 318° and 328°) in the last fractions of rosin spirit.

About one-half of rosin spirit consists of hydrocarbons boiling below 120°.

One of the most characteristic constituents of the lighter fractions of rosin spirit is the hydrocarbon *heptine*, $C_7H_{12}$, which appears to have the constitution of a *methyl-propyl-allene*. It boils at 103° to 104°, and has a sp. gr. of 0.8031 at 20°. Heptine is colourless, mobile, of characteristic odour, and is soluble in alcohol and ether. It absorbs oxygen very readily, and is without action on an ammoniacal solution of cuprous chloride or silver nitrate. By treatment with concentrated sulphuric acid it is polymerised, with formation of a *di-heptine* $C_{14}H_{24}$, boiling at 235–250°, and rapidly oxidising and resinifying in the air. By the action of water and air it is converted into a crystalline *heptine glycol*, $C_7H_{12}(OH)_2,H_2O$, soluble in water, alcohol, and ether. The crystals, as also the original hydrocarbon, when warmed with an acid (*e. g.*, hydrochloric, sulphuric, tartaric), give a series of colorations, the mixture passing through shades of yellow, red, green, and deep blue; and on adding this liquid to alcohol a magnificent green colour is communicated to it (G. H. Morris, *Trans.*, 1882, 41, 172). Rosin spirit itself does

[1] For a complete list of the constituents of rosin spirit, with their formulæ and b. p., see E. M. Holmes, *Pharm. Jour.*, 1899, 1, 99.
  G. H. Morris has published a valuable list of researches on rosin spirit prior to 1882 (*Trans.*, 1882, 41, 172).

not give the reaction distinctly, and Allen did not succeed in applying it to the detection of rosin spirit in turpentine oil.

## Rosin Oil

Rosin oil, or *resin oil*, is the heavier and less volatile portion of the product resulting from the dry distillation of colophony. The crude oil first obtained can be purified by washing with a small percentage of sulphuric acid, followed by treatment with lime-water and redistillation, with or without the aid of steam. A superior product is obtainable by redistilling the oil over solid sodium hydroxide, with the aid of a current of superheated steam. Lime-dust and other acid-removing agents have also been employed, and a very fine oil is said to be obtainable by mixing the crude oil with cottonseed oil prior to distillation.

**Commercial Varieties.**—Commercial rosin oil is a viscid liquid varying in colour from water-white to dark brown, and is sometimes opalescent from the presence of water. It generally exhibits a strong bluish or violet fluorescence, which is apparent even in its dilute ethereal solutions. The bloom is less marked in refined rosin oil, and can be destroyed more or less completely by exposure to air and sunlight, by treatment with hydrogen peroxide, by addition of nitrobenzene, nitro- or dinitro-toluene, dinitro-naphthalene, etc., or by heating with sulphur.

**Chemical Composition.**—The chemical composition of rosin oil is not perfectly understood. It often contains a notable proportion of *abietic acid*, or possibly abietic anhydride, but the greater part consists of a mixture of hydrocarbons of high b. p.[1]

The following results of analyses of samples of rosin oil examined in Allen's laboratory in 1886 show the variation in the character of the commercial article. The sp. gr. was determined by the bottle, the oils being too viscous to allow a plummet being satisfactorily used. The hydrocarbons were isolated as described on page 454,

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[1] According to A. Renard (*Compt. rend.*, 1887, 105, 865; 106, 856, 1086), about 80 % of the hydrocarbon constituents of rosin oil consists of *diterebentyl*, $H_{18}C_{10}$—$C_{10}H_{18}$. This substance forms a colourless oil which has a sp. gr. of 0.9688 at 18°, and boils at 343° to 346°. Its specific rotation is $+59°$. If a thin layer of diterebentyl is exposed to the air for some time, it absorbs about 10 % of oxygen and forms a sticky varnish. When treated in the cold with strong sulphuric acid, diterebentyl yields a monosulphonic acid as a brownish-black mass soluble in water, alcohol, and ether. Its solution is fluorescent, appearing brown by transmitted and green by reflected light.

If the fraction of rosin oil boiling between 300° and 360° be treated with sulphuric acid, the diterebentyl becomes polymerised or converted into the sulphonic acid mentioned above. If the oily portion be separated and distilled, the distillate contains *diterebentylene*, $C_{20}H_{32}$, and *didecene*, $C_{20}H_{38}$, which together form about 20 % of the hydrocarbons of rosin oil (A. Renard, *Compt. rend.*, 106, 1086).

and the resin acids subsequently recovered by acidifying the alkaline liquid.

| Description of sample | Sp. gr. | Resin acids | Hydro-carbons | Bromine absorption, dry | | Bromine absorption, wet | |
|---|---|---|---|---|---|---|---|
| | | | | Total | As HBr | Total | As HBr |
| Very pale refined oil........ | 0.990 | ...... | 96.9 | 110.0 | 11.8 | ...... | ........ |
| Pale oil, special............. | 0.982 | 6.4 | 93.9 | 105.1 | 4.8 | ...... | ........ |
| Pale sweet oil.............. | 0.979 | 1.1 | ........ | 63.0 | 4.7 | 56.5 | 13.6 |
| Ordinary oil................ | 0.985 | 17.8 | 81.2 | 138.5 | 9.7 | ...... | ........ |
| Common dark oil (not the commonest............... | 1.099 | 11.1 | 88.6 | 66.6 | 7.6 | ...... | ........ |
| Crude oil.................. | 0.990 | ...... | ........ | 60.8 | 3.9 | 47.0 | 11.2 |
| Pine oil................... | 0.986 | ...... | ........ | 73.9 | 5.1 | 51.9 | 8.9 |
| Ink oil.................... | 1.006 | ...... | ........ | ........ | ........ | ...... | ........ |

It will be observed that the bromine absorptions, as determined by the dry process, are extremely variable. There is also a wide divergence between the results by the dry and those by the wet process, and the absorptions of different samples are not even comparative. The figures obtained by the wet process are less than those yielded by the dry, while the reverse is the case with shale and petroleum products. The results were confirmed by repetition, and hence the anomalous figures are not errors of experiment.

An analysis of a commercial sample of rosin oil, made by J. Thompson, in Allen's laboratory, gave the following results:

| | % | Combining weight |
|---|---|---|
| Resin acids, weighed........................ | 15.72 | 289 |
| Resin acids, titrated (as $C_{20}H_{30}O_2$)............ | 16.91 } 98.62 | 302 |
| Unsaponifiable matter........................ | 81.71 } | |

**Uses.**—Rosin oil has a large legitimate employment as a lubricant, especially for machinery and wagon-wheels. It is used in the condition of rosin-grease, and in admixture with olive, rape, and other oils.[1] Mixed with rape oil, it has been employed for adulterating olive oil, and it is frequently added to the inferior kinds of boiled linseed oil. Castor oil has been systematically adulterated with rosin oil. Rosin oil is sometimes added to the denser kinds of mineral

[1] Information respecting the mode of manufacture of rosin oil, and the composition of various lubricants containing it, will be found in the *J. Chem. Soc.*, 1873, 26, 304, 305, and 1175, and also *J. Soc. Chem. Ind.*, 1902, 1336. The practical uses of rosin and rosin oil are also described in the *J. Soc. Chem. Ind.*, 1904, 23, 328.

lubricating oil, which are then treated with lime to make axle grease. It is also much used in making printers' inks mixed in varying proportions with linseed oil.

**Adulterants.**—This oil is sometimes adulterated with mineral oil, but it is more often the case that it is used to adulterate the more expensive oils, and mineral lubricating oils.

**General Properties.**—Rosin oil varies in colour from dark brown to colourless, according to the degree of refining to which it has been subjected. The refined product has but little odour at ordinary temperatures, but when strongly heated it gives fumes neutral or nearly neutral in reaction to wet litmus-paper, having a marked odour of resin, which burn readily with a smoky flame. When rosin oil is heated no distillate is usually obtained below 300°.[1] The taste is peculiar, and the after-taste is strong, nauseous, and highly characteristic. When treated with strong sulphuric acid as in Maumené's test for fixed oils, rosin oil usually gives a rise of 18° to 20° in temperature when 50 grm. are treated with 10 c.c. sulphuric acid (sp. gr. 1.84), and forms a reddish-brown liquid which separates into 2 strata. Nitric acid is sometimes without immediate action on rosin oil, but if the mixture be warmed, a violent reaction often ensues suddenly, and after cooling the oil is found to be converted into a more or less brittle red resin. When agitated with one-third of their volume of fuming hydrochloric acid, most samples of rosin oil gradually acquire a dark and ultimately black colour. Chlorine and bromine act somewhat violently on rosin oil. The proportion of bromine absorbed is very variable.

**Specific Gravity.**—Crude rosin oil has a sp. gr. ranging from 0.96 to 1.1, but when refined the figures are much more constant, and vary only from 0.97 to 0.99.

**Solubility.**—Rosin oil is insoluble in water, and only slightly soluble in alcohol. It is miscible in all proportions with fatty oils, mineral oils, ether, chloroform, carbon disulphide, turpentine oil and petroleum spirit. The greater solubility of rosin oil in glacial acetic acid compared with that of mineral oil has been suggested by Valenta and Feigerle as a means of its detection in mixtures. Demski and Morawski used acetone for the same purpose. These methods do not always give very satisfactory results.

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[1] However often rosin oil be distilled, the product always contains a small quantity of terpenoid substances, which are probably produced by depolymerisation of the heavier hydro-carbons by a process of "cracking," similar to that undergone by the hydrocarbons of petroleum under the same conditions.

**Optical Properties.**—Rosin oil is strongly dextrorotatory, and this value varies from $+30$ to $+50$ for the sodium ray. To render highly coloured rosin oil fit for optical examination, Valenta treats it with potassium ferrocyanide and then filters.

**Identification.**—Renard has observed that anhydrous stannic chloride develops a violet coloration with rosin oil. Allen found it more convenient to employ stannic bromide than stannic chloride, and that the test is much more delicate and under control if free bromine is also present and the oil and reagent are previously dissolved in carbon disulphide. The stannic bromide is prepared by allowing bromine to fall drop by drop on granulated tin contained in a dry flask immersed in cold water. The addition is continued until the permanent coloration of the product shows that the bromine is in excess. A further moderate addition of bromine is then made, and the liquid is then diluted with three or four times its volume of carbon disulphide, in which the stannic bromide is readily soluble. To employ the reagent, which when thus prepared appears to be perfectly stable, a few drops of the sample should be placed in a dry test-tube and dissolved in about 1 c.c. of carbon disulphide. The bromide reagent is then gradually added, when if rosin oil be present the liquid will rapidly acquire a fine violet coloration, which in the case of pure rosin is so intense as to necessitate dilution with carbon disulphide before the colour is perceptible. On standing for some time, a deposit of violet colour is formed at the bottom of the tube, and if the remaining liquid be poured off and the residue be warmed with a little carbon disulphide, a violet or purple solution of great purity of tint may be obtained. This mode of operating is especially useful in the presence of foreign oils or impurities which disguise the colour due to rosin oil. In the presence of much mineral oil Allen found it a good plan to first mix the sample with a solution of stannic bromide in carbon disulphide, and then add, drop by drop, a solution of bromine in carbon disulphide, by which means the violet coloration may often be obtained unobscured by any colour produced by the mineral oil.

The violet substance to which the coloration is due appears to be permanent in the air, but the colour is destroyed by addition of alcohol, ether, ammonia, or water.

Chloroform may be substituted for carbon disulphide in the foregoing test.

Instead of dissolving the oil in carbon disulphide it may be dissolved in glacial acetic acid, and the greater solubility of rosin oil than mineral oils in this menstruum affords a means of applying the test to mixtures of the two in a very advantageous manner. Thus, if the sample to be tested be shaken in the cold with twice its volume of glacial acetic acid, and the acid layer separated and tested with a solution of stannic bromide and bromine in carbon disulphide or chloroform, a fine violet coloration will be produced if rosin oil be present. The coloration produced in acetic acid solution appears to be of decidedly bluer shade than that obtained when carbon disulphide is used as the solvent for the oil, but the tint in the latter case varies considerably with the proportion of the reagent used, a large excess having a tendency to produce reddish tints.

A test for rosin oil in the presence of mineral and saponifiable oils has been based on Storch's reaction with sulphuric acid, but in its original form the test is fallacious in presence of cholesterol, etc. As modified by T. Morawski, the sample is dissolved in acetic anhydride, with the aid of gentle heat, the liquid cooled, and a few drops of sulphuric acid of 1.53 sp. gr. allowed to flow down the side of the test-tube, so as not to mix with the contents. In presence of rosin oil or rosin, a violet-red coloration will be produced at the point of contact. Holde modifies the test by simply shaking up the oil with sulphuric acid of 1.53 sp. gr. In a subsequent paper he increases the strength of the acid to 1.624 sp. gr. which is stated to give the reaction more promptly. The different modifications of the test have been investigated by A. Grittner (*Zeit. angew. Chem.*, 1891, **4,** 265), who considers the weaker acid preferable, since with the stronger, other oils are liable to give colorations which more or less obscure that due to rosin oil. For fatty oils containing but a small proportion of rosin oils, Morawski's method is preferable, but with dark oils Holde's is the better. Morawski's test is inapplicable to dark lubricating mineral oils. In the possible presence of resins, such as colophony or shellac, it is necessary to saponify the oil and test the unsaponifiable matter. A modification suggested by Holde (*Mitt. Königh. Vers.-Anst., Berlin*, **6,** 88) is to agitate the oil to be tested with alcohol, and apply the test to the separated alcoholic liquid or the residue left on its evaporation. By careful procedure, very small proportions (*e. g.*, 1%) of rosin oil can be detected by the above test.

From experiments made in A. H. Allen's laboratory, J. Thompson considered the following method of operating to be the most satisfactory: About 1 c.c. of the oil to be examined is placed on a porcelain crucible lid and 2 c.c. of acetic anhydride well mixed with the oil and warmed. In the case of oils not completely soluble in acetic anhydride, the mixture should be made in a test-tube, and the lower layer separated and placed on the porcelain lid. A drop or two of sulphuric acid (sp. gr. 1.53) is then added to the acetic anhydride solution, when a beautiful purple coloration will be obtained in the presence of rosin oil, rosin, etc. When the test was performed as above described on a flat or slightly concave porcelain surface, better results were obtained than by pouring the acid down the side of the test-tube.

The colorations obtained by the stannic bromide and acetic anhydride and sulphuric acid tests for rosin oil are mainly due to the hydrocarbon oils present, as is shown by the following results obtained in A. H. Allen's laboratory:

|  | Resin acids | Unsaponifiable matter |
|---|---|---|
| Stannic bromide............ | Faint coloration on standing. | Strong purple colour. |
| Acetic anhydride and sulphuric acid (1.53 sp. gr.). | Faint purple, fading immediately. | Brilliant purple, fading in a few minutes. |

Another colour test for the detection of rosin oil in the presence of mineral oils, etc., has been described by G. Halphen (*J. Pharm. Chim.*, 1903, **16,** 478), and is based on the fact that rosin oil gives an intense violet and blue coloration with a solution containing bromine and phenol, whilst mineral oils give only a brown colour with a slight violet fluorescence. The presence of water or alcohol interferes with the test. The substances causing the coloration are apparently identical with those giving the Liebermann reaction, and these can be extracted with strong alcohol, when the dry residue gives the colour with greater intensity. The test is carried out as follows: A drop of the oil to be examined is thoroughly mixed with 2 c.c. of a solution of crystallised phenol in carbon tetrachloride (1 in 2) in a porcelain crucible, and bromine vapour, from a flask containing bromine dissolved in carbon tetrachloride (1 in 4), allowed to fall into the crucible. The reaction is complete in from

5 to 10 seconds.    Comparison tests with samples of known composition should be made, when less than 10 % of rosin oil may be detected. Chinese wood oil gives a carmine coloration with violet or blue tinge, and marine animal oils give a carmine colour.    Other oils give either much fainter or only indefinite reactions, among the latter being most vegetable oils.

The detection of rosin oil in fatty oils is based on its isolation by the method described in Vol. II, page 94 and its subsequent identification by its taste, odour on heating, sp. gr., optical activity, reaction with stannic bromide, and formation of a grease with slaked lime.    Some of these tests are applicable to the original mixture of fatty and rosin oils.    If the accurate estimation of the rosin oil be desired, it will often be necessary to add to the weight of the hydrocarbons or ether residue that of the resin acids, after separation from the fatty acids as described in Vol. II, page 94.

The detection of rosin oil in admixture with the mineral lubricating oils may be effected with tolerable ease and certainty, but the positive recognition of a moderate proportion of mineral oil in such a mixture is more difficult.    Any optical activity of the sample or purple reaction with stannic bromide affords definite proof of the presence of rosin oil, and in many cases its existence is evident from the taste of the sample and its odour on heating.    A high sp. gr. and bromine absorption, and a violent reaction with nitric acid, also afford strong evidence of the presence of rosin oil.

**Estimation.**—Valenta and Feigerle (*Dingl. polyt. J.*, **253,** 418); and Demski and Morawski (*Dingl. polyt. J.*, **258,** 82) have each suggested methods for the detection and estimation of rosin oil in mineral lubricating oils. Lewkowitsch considers the former method, which can be carried out as follows, the most reliable, although the nature of various petroleums considerably affects the accuracy of the result: 2 c.c. of the oil should be treated with 10 c.c. of glacial acetic acid (sp. gr. 1.0562 at 15°), and heated for five minutes to 50° in a loosely-corked test-tube immersed in a water-bath.    The mixture is then passed through a small filter and the middle portion of the filtrate collected.    A weighed quantity of the filtrate is then titrated with standard alkali and phenolphthaleïn, whereby the weight of acetic acid present can be calculated, and the difference between the amount thus found and the weight of the portion of filtrate operated on gives the weight of oil dissolved

by the acetic acid in that quantity of the filtrate.[1] When examined in this manner, the solubility of mineral lubricating oil (apparently from petroleum) varied from 2.67 to 6.50 grm. for 100 grm. of glacial acetic acid, whilst a sample of crude rosin oil of 1.0023 sp. gr. showed a solubility of 16.87%. The solubility of a mixed sample does not, however, increase regularly with the proportion of rosin oil present.

## Detection of Adulterants

**Mineral Oil.**—H. Holde (*Mitt. Kgl. techn. Versuchsanstalt, Berlin*, 1902, 39) has suggested a method which has proved successful for the detection of even small quantities of mineral oil in rosin oil. The test is carried out as follows: 10 c.c. of the oil under examination are vigorously shaken in a separating funnel with 90 c.c. of 96% alcohol (by weight). If any noticeable quantity of the oil remains undissolved, then mineral oil in considerable quantities is undoubtedly present. This conclusion can be confirmed by first allowing the undissolved oil to settle and, after washing it with a small quantity of 96% alcohol, determining its refractive index. Mineral oils have a refractive index below 1.5330 at 15° to 20°. In doubtful cases the undissolved oil can be further treated in the following manner, and again tested in the refractometer. If only traces of oil remain undissolved by the preliminary treatment with 99% alcohol (by weight), the alcoholic solution is diluted with sufficient water to cause a very apparent milkiness in the liquid. After the solution has been allowed to stand at least 24 hours, the alcoholic solution is separated from the precipitated oil drops, which should not have a greater volume than 1 c.c. The oil is then washed with a few c.c. of 96% alcohol, and the residue is again dissolved in 20 c.c. of 96% alcohol at ordinary temperature. From this solution by the addition of water a few drops of the oil are again precipitated, and after the solution has been allowed to stand these oil drops are separated, washed first with cold alcohol and then with hot alcohol in a small glass evaporating dish. When the alcohol has been evaporated and the oil cooled the refractive index of the residue is determined. If a lower figure than 1.5330 is found, mineral oil was present.

**Rosin grease** is made by stirring together rosin oil and slaked lime. One method of preparation consists in stirring the rosin oil

[1] The presence of rosin acids in the rosin oil would alter its solubility, and also make the estimation of the acetic acid inaccurate. It would be better to neutralise the greater part of the acetic acid, dilute with water, and extract the rosin oil by agitation with ether.

with about three-fourths of its weight of slaked lime made into a cream with water. The mixture rapidly solidifies, extruding the superfluous water, which is run off, and the grease is then diluted by gradually stirring in a further quantity of oil, until the desired consistence is attained. The oil used for diluting may be rosin oil, petroleum oil, or neutral coal-tar oil ("grease oil"). Rosin grease is also made by mixing dry slaked lime with rosin oil, without water, or by mixing the lime with mineral or coal-tar oil, and subsequently by adding the rosin oil. Barium sulphate, gypsum, whiting, and other make-weights are also added Cheap greases are thus prepared, which are used to lubricate the iron axles of colliery trucks and ordinary road vehicles. Rosin grease rapidly acetifies by heat and friction, and hence is not adapted for the lubrication of brass bearings.

The formation of rosin grease has been attributed by E. J. Mills to a supposed property possessed by the unsaturated hydrocarbons contained in rosin oil of combining directly with lime and other bases ("Destructive Distillation," 4th edition, 1892, p. 97). The true explanation is that crude rosin oil invariably contains a considerable percentage of resin acids (undecomposed colophony), which have distilled over with the hydrocarbons, and it is the combination of these acids with the lime which is the real cause of the formation of rosin grease. According to L. Archbutt, refined rosin oil, which has been freed from resin acids, is incapable of forming a grease with lime; while on the other hand, the larger the percentage of resin acids contained in the crude rosin oil, the stiffer the grease which can be formed.[1]

| Description of rosin oil | Resin acids |
|---|---|
| A. "Pale refined" | 0.14% |
| B. "Medium" | 5.80% |
| C. "Hard-run" | 21.30% |

The acids extracted from each sample were quite hard and brittle.

20 grm. or each of the above oils was stirred with about 45 c.c. of a cream of lime, containing about 15 grm. of slaked lime. The mixture made from sample

[1] The percentage of resin acids in 3 samples of commercial rosin oil was estimated by Archbutt by dissolving a weighed quantity of each oil in ether, shaking out with sodium, hydroxide and weighing the resin acids recovered from the hydroxide solution. The results above (table) were obtained.

A did not perceptibly thicken on stirring and formed no solid grease on standing. Both the other mixtures set. The hydrocarbons isolated from sample C by dissolving the oil in ether, agitating the liquid with sodium hydroxide, and evaporating the separated ethereal layer, showed no tendency to emulsify when treated with milk of lime, even after a long period.

Archbutt and Deeley give the following analyses of 2 samples of rosin grease: For methods of analysis see Vol. III.

|  | A | B |
|---|---|---|
| Hydrocarbon oil | 87.7% | 86.6% |
| Resin | 3.7% | 7.0% |
| Slaked lime ($CaH_2O_2$) | 6.4% | 4.5% |
| Water, etc. (by difference) | 2.2% | 1.9% |
|  | 100.0 | 100.0 |

# COPALS

**Occurrence.**—The copals comprise a number of recent, partly fossilised, and fossil resins, found in nearly all tropical and subtropical countries of the world. Africa is the home of the hardest and most prized varieties, but medium, hard, and soft resins are also found in that continent. There is much doubt as to the actual origin of the various resins.

Zanzibar copal is undoubtedly furnished by the tree *Trachylobium verrucosum;* Kauri comes from *the Dammara australis*, and the South American resins are derived from *Hymenœa courbaril*. Large quantities of copals are also obtained from Asia, and the west coast of Africa, but the actual botanical sources are not known.

**Commercial Varieties.**—The commercial copals may be classed into 5 groups.

(*a*) East African copals—Zanzibar, Madagascar, Mozambique, and Lindi.

(*b*) West African copals.

(*c*) Manila copals.

(*d*) Kauri copals.

(*e*) South American copals.

Although there are many varieties of East and West African copals, it is only possible to differentiate between them in very few cases. The East African resins shipped from Zanzibar are characterised by a peculiar indented surface commercially known as the "goose skin." These resins are cleaned and graded according to colour, etc., at the place of export.    The West African varieties arrive at the ports of Europe in their natural condition.    Benguela copal, red Angola copal, pebble copal, and Sierra Leone copal each possess characteristics which enable the expert to identify them.    At the copal washing establishments in Europe the natural resins are brushed and treated with alkaline solutions of varying strengths to remove the oxidised crust with which they are more or less coated.    The cleaned product is then graded according to general appearance, size, colour, hardness, etc.    By this treatment, resins from various sources with similar characteristics are batched together, and for commercial purposes are given a name which appears most suitable, irrespective of the original source.    The Manila copals include all the Asiatic fossil resins at present known.    Some have special characteristics, but others are so like gum Kauri that it is almost impossible to distinguish them from the latter: the slight difference in the smell affords a clue to the expert, but many varieties of this copal cannot be differentiated.    They are at times forwarded to Europe in their natural state, but more often they are washed at some central station and classified according to their physical properties.    South American copals are not important commercial articles.    The so-called Brazilian copal of commerce has all the properties of the West African copals; very probably it is derived from this source.

**Chemical Composition.**—As previously stated, many of the resins are of unknown origin, and the methods adopted for obtaining these substances for the industries increase the difficulty of determining the source from which any given resin has been obtained; hence it is often quite impossible to trace the actual resins on which various chemists have reported, and their work consequently loses much of its value.

Tschirch and Stephan have investigated the chemistry of an authentic specimen of Zanzibar copal, which they found to contain the following compounds: 80% of *trachylolic acid*, $C_{54}H_{85}O_3(OH)$-$(COOH)_3$; about 4% of an isomeric acid, *isotrachylolic acid;* 2 indif-

ferent neutral resinous substances, *α-copalresene* and *β-copalresene;* and about 10% of *essential oil.* The ash was only 0.12%.

Two copals,[1] stated by the authors to be of undoubted origin, belonging to the copaiba copals of Tschirch's system, have been examined by Tschirch and A. Engel (*Archiv. Pharm.*, 1908, **246,** 293–305).

(*a*) The Congo copal contained 48 to 50% of amorphous congo-copalic acid, $C_{19}H_{13}O_2$; 22% of congo-copalolic acid, $C_{22}H_{34}O_3$, also amorphous; about 5 or 6% of α-Congo-copal resene soluble in ether; 12% of β-Congo-copal resene, insoluble in ether, and from 3 to 4% of fragrant essential oil.

(*b*) The Benguela copal contained from 43 to 45% of amorphous bengu-copalic acid, $C_{19}H_{30}O_2$; 22% of bengucopalolic acid, $C_{21}H_{32}O_3$; from 4 to 5% of α-bengucopaloresene, soluble in ether; and 14 to 16% of bengucopaloresene, $C_{22}H_{36}O_2$, insoluble in ether; and 3 to 4% of essential oil.

The different varieties of copal have been the subjects of numerous investigations by Tschirch and his collaborators, whose results are tabulated on following page.

**Uses.**—The copals are chiefly used in the varnish and kindred industries. They are first subjected to destructive distillation. After a certain percentage of water, gas, and oil, varying from 12 to 25%, has distilled off, the resin becomes soluble in linseed oil and turpentine. Various methods have been suggested to reduce this loss, but commercially they have not yet been adopted.

**Adulterants.**—Poor-quality copals are often mixed with the harder and more prized varieties. The lowering of the melting point may afford some information. Speaking generally, the manufacturer must at present depend largely upon his practical tests to

[1] The Congo copal was composed of irregular angular pieces with a light yellow to brownish-red colour, coated with a thin oxidised resin crust. It broke with a glassy fracture and emitted a slight odour of copaiba balsam. When heated in a capillary tube the following changes were observed: at 90°–92°, became brownish-yellow; 105°, lost powdered appearance (lower m. p. Bamberger); 125°–130°, bubbles of gas were evolved; 175°, became clear. 48% of the resin was soluble in alcohol.
*Analytical Values.*—Acid value (direct), 117.7
                Acid value (indirect), 124.8
                Saponification value (cold, 24 hrs.), 138.6
                Saponification value (hot, 1 hr.), 152.6
                Saponification value (hot, 2 hrs.), 149.2
The Benguela copal examined was a mixture of various-sized flat, globular, and stalactitic pieces, light and dark brown in colour. An oxidised resin crust was visible in some parts of the nodular surface. 56% of this resin is taken up by alcohol. Lower m. p., 106°–108°; higher m. p., 156°–168°.
*Analytical Values.*—Acid value (direct), 112–114.8
                Acid value (indirect), 117.6–120.4
                Saponification value (cold), 117.6–123.2
                Saponification value (hot), 120.4–123.2

## COMPOSITION OF COPALS

| | Zanzibar copal | Manila copal | (New Zealand) Kauri bush copal |
|---|---|---|---|
| Botanical origin | (Fossil and recent) *Trachylobium* and *Hymenaea* species. | *Dammara orientalis*. | (Fossil) *Dammara Australis*. |
| **Resin Acids** | | | |
| A. Soluble in Am. carbonate: | | | |
|   *a.* Crystallisable | ......... | Mancopalic, $C_8H_{12}O_2$. M. p. 175°).K₁I₁.$(a)_D = +56°$ } 4% Mancopalenic, $C_4H_{14}O_2$. (100–105°)K₁I₁. | Kauric or Kaurinic, $C_{10}H_{16}O_2$ (192°).K₁I₁.$(a)_D + 51.7$:1.5% |
|   *b.* Amorphous | ......... | Mancopalolic, $C_{10}H_{18}O_2$; 75 to 80%. | |
| B. Insoluble in Am. carbonate: | | | α- and β-kaurolic acids, $C_{12}H_{20}O_2$. (48 to 50%). Kaurinolic and Kauronolic acids. (20–22%). |
|   *a.* Crystallisable | ......... | (85–90°)K₁I₁. | |
|   *b.* Amorphous | ......... | (83–88°)K₁I₁. | |
| α-acid, ppted. by alcoholic lead acetate | Trachylolic, $C_{66}H_{58}O_8$, 80% (sphæro crystals, 168°).K₂ (probably). | | (α-Kaurolic (81–83°). Kaurinolic, $C_{17}H_{26}O_2$.(128–130°). |
| β-acid, not ppted. by alcoholic lead acetate | Isotrachylolic (106°).K₂. 4%. | | β-Kaurolic (85–87°). Kauronolic, $C_{12}H_{24}O_2$. (86–89°). |
| Indifferent Resins | α-copalresene (75 to 77°) $(a)_D$(in alcohol), +12.5° } $C_{38}H_{38}O_4$ 6%. β-copalresene (Decomposes at 140° without melting.) | Mancopaloresene, $C_{20}H_{34}O$. } 12% (80–85°). | Kauroresene, 12%, 63 to 65° (impure). |
| **Essential Oil** | | | |
| A. Readily volatile with steam | 9%. | (B.p. 165–170°); 6%. Sp. gr. 0.840. | (150 to 160°); 12.5%. Sp. gr. 0.835. |
| B. Tailings | About 0.5%. | 3% | Small. 0.5 to 2% |
| **Minor Constituents** Bitter principle, alkaloid, succinic acid, colouring matter, water and impurities | | | |
| **Reference** Original | Arch. Pharm., 1896, p. 552. 1897, I, 92, | Arch. Pharm., 1902, p. 202. 1902, I, 478. | Arch. Pharm., 1901, p. 145. 1901, I, 308. |
| Abst. Jour. Chem. Soc. | | Another sample of Manila copal contained no acids soluble in ammonium carbonate. | |

obtain definite information regarding the quality of the resin under consideration.

**General Properties.**—The copals vary in colour from white through shades of yellow and red to brown and brownish-black. The same variety is often found in colours ranging from white to deep red. The natural fossil, and semi-fossil resins are mostly covered with an oxidised crust containing much mineral matter. This can be removed by treatment with alkaline solutions. When broken they generally show a conchoidal fracture and the new fracture has a lustrous appearance. Some of the resins emit characteristic odours, particularly when crushed, whereas, for example, Zanzibar copal is odourless.

(*a*) *Zanzibar Copal.*—This copal has a characteristic surface covered with a number of small and large excrescences closely packed together, commercially known as the "goose skin." When the naturally opaque crust consisting of sand and atrophied resin is removed, the internal part of each piece is clear and transparent, and the colour varies from light yellow to brownish-red. Various brands of this resin are found in commerce, designated by letters. W stands for white, R represents red, while the letters A, B, C, etc., denote the size of the pieces; *e. g.*, W A means white, large. Transparent flat plates are generally the best form. They vary in size from 0.25 to 1.5 in. in width and from 0.167 to 0.5 in. in thickness. Zanzibar copal breaks with a flat fracture which is mostly brilliant in appearance, but the best varieties show a fracture half brilliant and half matt. This resin breaks between the teeth and does not agglutinate.

(*b*) *Yellow Benguela Copal.*—Benguela copal is found in uneven lumps varying from 4 inches to 10 inches in diameter. These pieces are covered with protuberances, and in places have crevice-shaped indentations extending inward as far as one-third of the lump. This outward appearance is characteristic, and possessed by no other copal. When in the raw state it is covered more or less with an oxidised crust which is white, yellowish, or yellow in colour. It breaks with a brilliant fracture, is transparent, and has a light yellow to yellow, seldom a reddish tint.

(*c*) *Red Angola copal* is found in more or less round pieces, coated with a red oxidised resin crust covering regular protuberances on the surface of the resin. After removal of the crust the resin is clear and transparent.

(*d*) *Pebble Copal*.—This resin, as its name implies, has the appearance of small pebbles varying in size from a pea to a pigeon's egg, and covered with a whitish coating. The colour varies from white to yellow, sometimes to a reddish yellow. The resin is half transparent and breaks with a glassy fracture.

(*e*) *Sierra Leone copal* is found in pieces varying in size from a pea to that of the fist. They have the form of either balls or drops, and the surface is in some cases uneven and in other cases quite smooth. The colour varies from colourless to a light yellow; other pieces have a rosy-red or sea-green appearance. It is mostly clear and transparent, but impure pieces are milky and half transparent or opaque. An oxidised resin crust is rarely found on the natural resin and in any case it is only slightly apparent. This copal breaks with a conchoidal fracture and emits a spicy odour, which is more noticeable when the resin is melted.

(*f*) *Manila Copal*.[1]—This resin is found in large, irregular, angular milky pieces, and is mostly covered with a white or yellowish coating. It varies from a yellow to a honey-yellow colour, but brownish-yellow, smoky-grey, greenish and blackish pieces are also found. It breaks with a conchoidal fracture, which is matt in appearance. It is transparent to semi-transparent.

(*g*) *Kauri Copal*.—This copal is found in rather large irregular, angular or round pieces which have externally a dull appearance, and are often coated with a whitish crust. The colour of the resin varies considerably, and this is often observable in one and the same piece. It is mostly whitish, yellow, or brownish-yellow in colour, but smoky-grey, light and deep brown pieces are also found. The transparency varies in different parts of the same piece. Striated, smoky, and cloudy portions are to be found on nearly every lump. The Kauri resin from New Zealand is generally brown in colour, whilst the New Caledonian varieties are mostly yellow or white. The surface of all Kauri copals are covered with an opaque crust as thick as the finger. In the New Zealand resins this crust is mostly chalky, whilst the New Caledonian resins have a brown or blackish colour.

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[1] Manila Copal, C. Coffigner (*Bull. Soc. Chim.* 1907 (4) 3, 453). Manila copal occurs in 3 varieties—hard, semi-hard, and friable. The hard variety occurs in large pieces, varying in colour from dull white to brown. The pieces break easily with a brilliant fracture; some pieces are milky inside; the odour is aromatic. The white form had the sp. gr. 1.065, m. p. 190°, softening at 80°. Acid value, 72.8. Saponification value, 87. The friable variety, which unlike the above is completely soluble in alcohol, occurs in aromatic pieces of varying colour which break readily with a fairly brilliant fracture. Sp. gr. 1.060, m. p. 120°, softening at 45°. Acid value, 145.2. Saponification value, 185.1.

When chewed this gum clings to the teeth. The taste is pleasant and the smell aromatic.

**Hardness.**—Generally speaking, the greater the hardness the more valuable the copal. This generalisation does not hold good for gum Kauri. This resin has been used extensively in the varnish industry, not only because of the good results obtained, but also for the ease with which it can be manipulated by the varnish manufacturers. There are other resins which melt at a lower temperature, but they have peculiar properties and are not so easy to work. Böttler has given the following scale of hardness in which Zanzibar copal is taken as the standard.

| No. | Copal | No. | Copal | No. | Copal |
|-----|-------|-----|-------|-----|-------|
| 1 | Zanzibar copal. | 6 | Sierra Leone copal, old. | 11 | Manila copal. |
| 2 | Mozambique copal. | 7 | Yellow Benguela copal. | 12 | White Angola copal. |
| 3 | Lindi copal. | 8 | White Benguela copal. | 13 | Kauri copal. |
| 4 | Red Angola copal. | 9 | Cameroon copal. | 14 | Sierra Leone (new). |
| 5 | Pebble copal. | 10 | Congo copal. | 15 | Hymenæa copal. |

**Specific Gravity.**—The copals most frequently met with have a sp. gr. ranging between 1.03 to 1.07. This number holds good when the sp. gr. is taken directly, but when crushed and freed from air bubbles the gravity of the copals increases slightly. The difference thus observed is considerable for the softer varieties of copal and very small for the harder varieties (Böttler).

| Copal | A<br>Sp. gr. at 15°<br>of copal<br>freed from<br>air | B<br>Sp. gr. at 15°<br>of natural<br>copal | A—B | Position in<br>table of<br>hardness |
|-------|------|------|------|------|
| Zanzibar................. | 1.0636 | 1.0621 | 0.0015 | 1 |
| Lindi................... | 1.0695 | 1.0685 | 0.0010 | 3 |
| Red Angola............. | 1.0820 | 1.0680 | 0.0140 | 4 |
| Brazilian............... | 1.0830 | 1.0690 | 0.0140 | .......... |
| Cameroon............... | 1.0800 | 1.0650 | 0.0150 | .......... |
| Kauri.................. | 1.1096 | 1.0480 | 0.0516 | 13[1] |
| Manila................. | 1.1280 | 1.0690 | 0.0590 | 11[1] |
| Hymenæa............... | 1.1310 | 1.0690 | 0.0620 | 15 |

[1] In Andés scale of hardness Kauri stands before Manila.

From this table it appears that Hymenæa copal, Manila copal, and Kauri copal belong to the poorer qualities; Cameroon and red

Angola take up an intermediate position, and Zanzibar and Lindi copals take first place. Even from this table, Brazilian copal does not appear to be a South American variety, but related to the West African copals.

**Melting-point.**—Böttler stated that all copals could be melted between 95° and 305°, but further experiments have proved that specimens of Lindi and Zanzibar copals do not melt below 340° and 360°. Böttler takes that temperature as the m. p. when the material begins to liquefy, whereas Bamberger takes two temperatures: *a.* When the opaque substance in a capillary tube becomes homogeneous; *b.* when the resin liquefies completely, at times with decomposition.

| Copal | M. p., Böttler | M. p., Bamberger | | Copal | M. p., Böttler | M. p., Bamberger | |
|---|---|---|---|---|---|---|---|
| | | *a* | *b* | | | *a* | *b* |
| Hymenæa........ | 95° | 77° | 115° | Congo copal...... | 180° | ..... | .......... |
| Cameroon........ | 108° | 96° | 110° | Sierra Leone...... | 185° | ..... | .......... |
| Cameroon........ | 108° | 110° | 120° | Pebble copal...... | 220° | ..... | .......... |
| Manila.......... | 112° | 103° | 120° | White Angola..... | 245° | 143° | 340° |
| Manila.......... | 135° | ..... | .......... | Lindi............ | 246° | 158° | 330°–360° |
| Kauri........... | 126° | 111° | 115°–140° | Zanzibar......... | 259° | ..... | .......... |
| Yellow Benguela.. | 170° | ..... | .......... | Zanzibar......... | 265° | ..... | .......... |
| Wite Benguela.... | 175° | ..... | .......... | Red Angola....... | 305° | ..... | .......... |

**Solubility.**—The usual solvents can be applied to the copals: Kauri, Borneo, and Manila copals are to the greater part soluble in 96% alcohol. White and yellow Benguela copal, red Angola, Congo, and Cameroon copals can be brought more or less into solution by first heating to 100° for 48 hours, powdering, then mixing with sand or powdered glass, allowing to stand with ether in which they swell, then adding the necessary quantity of warm alcohol. Sierra Leone and Zanzibar copals require long digestion. Manila copal, after it has been powdered and exposed, dissolves in ether; 40% of Sierra Leone copal dissolves in alcohol, but Zanzibar copal is scarcely affected. Spirits of turpentine has no immediate action on these resins, but when oxidised turpentine is used all copals are dissolved more or less, and Sierra Leone copal completely. Amyl acetate is a good solvent for these resins, but its use is marred by its odour. Amylic alcohol is a very active solvent for Kauri and Manila, but it scarcely affects the harder varieties. Alkaline solutions attack all copals—soft varieties are easily saponified at a low

heat, whilst the harder sorts are strongly attacked. Angola copal is completely dissolved.

**Analytical Data.**—Many workers have attempted to establish analytical limit constants for the copals, but as yet the values obtained have varied within such wide limits that the results cannot be employed in their commercial valuation.

Lippert and Reissiger (*Zeit. angew. Chem.*, 1900, **13,** 1047) obtained the following results in the analysis of various commercial samples. For the estimation of the acid value, 1 grm. of the sample was treated with 10 c.c. of chloroform, and after standing some hours 25 c.c. of alcohol was added. If the copal was not dissolved by this treatment, ether, or a mixture of alcohol and ether, was used, and when solution was complete, the liquid was titrated with N/2 alcoholic potassium hydroxide, using phenolphthalein as indicator. The saponification value was obtained by heating the copal with alcohol and ether (not chloroform), adding excess of standard alcoholic potassium hydroxide, and proceeding as usual. The ester value is the difference between the acid saponification values. In certain cases, such as Manila copal, it probably represents lactonic compounds and not esters.

| Variety of copal | Acid value | Saponification value | Ester value | Remarks |
|---|---|---|---|---|
| Angola, white............ | 59 to 61 | ........... | ........ | R. Williams[1] found acid value 57. |
| Angola, red.............. | 90 | 148 to 152 | 58 to 62 | Schmidt and Erban[2] found saponification value 148. |
| Angostura............... | 48 | ........... | ........ | Fine glassy yellow lumps. |
| Benguela, select......... | 61 to 62 | 111 to 126 | 50 to 64 | Clear yellow balls. |
| Benguela, ordinary....... | 84 to 87 | ........... | ........ | Contains dirt. |
| Brazil, select............ | 153 to 158 | 148 to 157 | 1 to 5 | Splendid pale yellow balls. |
| Cameroon............... | 106 to 109 | ........... | ........ | Easily soluble in alcohol. |
| Dammar................ | 33 to 35 | ........... | ........ | Completely soluble in oil of turpentine. |
| Kauri, select............ | 81 | ........... | ........ | Not quite transparent. |
| Kauri, light ordinary..... | 63 to 64 | 95 to 109 | 32 to 39 | Williams found saponification value 64.2. |
| Kauri, dark............. | 66.5 to 70 | ........... | ........ | |
| Madagascar............. | 60 | ........... | ........ | Easily soluble in alcohol-chloroform. |
| Manila, select........... | 103 to 111 | 147 to 152 | 44 to 50 | Hard, easily soluble in alcohol. |
| Manila, soluble in alcohol. | 144 to 148 | ........... | ........ | Soft, easily soluble in alcohol. |
| Sierra Leone............. | 78 to 82 | ........... | ........ | Small light balls. |
| Zanzibar................ | ........... | 88 to 102 | ........ | Characteristic "goose-skin" appearance. |

[1] Williams' results will be found in detail in *Chem. News*, 1888, **58,** 224.
[2] Schmidt and Erban's results are recorded in *Zeit. angew. Chem.*, 1889, **1,** 35. Coffignier has published further constants and solubility values for Zanzibar and Madagascar copals (*Bull. Soc. Chem.*, 1903, **29** (ii), 581).

Other investigators[1] have obtained values differing widely from those given table on preceding page. It is very probable that the varying methods employed in the estimation of the values may partly account for the discrepancies, but the complex composition of the copals, and the doubtful relationship existing between the name and origin of the commercial resins, affords the more probable explanation.

J. Marcusson and G. Winterfeld suggest the following method for the estimation of the acid value: 3 to 4 grm. of the finely powdered resin are heated for a short time with 200 c.c. of a mixture containing equal parts of benzene and neutral absolute alcohol. When cold, the solution, plus any undissolved resin, is titrated with N/10 alcoholic potassium hydroxide in the presence of phenolphthalein.

They obtained the results given on p. 277 by this process.

R. A. Worstall has published some valuable results obtained with the fossil resins (*J. Amer. Chem. Soc.*, 1903, **25**, 860). He ascertained the "acid" value by Dieterich's indirect process. The iodine values obtained by this observer (by treating 0.2 grm. of the sample and 10 c.c. of chloroform with 50 c.c. of Hübl solution for 18 hours in the usual way) were as follows:—

| Copal | No. of samples examined | Iodine value | |
|---|---|---|---|
| | | Max. | Min. |
| Kauri.......................................... | 43 | 170 | 74 |
| Manila........................................ | 19 | 148 | 104 |
| Pontianac.................................... | 2 | 142 | 119 |
| Zanzibar...................................... | 2 | 123 | 115 |
| Mozambique.................................. | 1 | 136 | |
| Madagascar.................................. | 1 | 126 | |
| West African................................ | 8 | 143 | 122 |
| Sierra Leone................................ | 2 | 105 | 102 |
| Brazilian..................................... | 3 | 134 | 123 |

Schmidt and Erban (*Zeit. angew. Chem.*, 1889, **1**, 35) found, in the case of *melted* Angola copals, 93.6 and 25.2 for the acid and ester

[1] Coffignier, "Properties of Several African Copals." *Revue de Chimie industrielle*, **16**, 103–106.
Coffignier, "Several American Copals." *Bull. Soc. Chim.*, 1906 [3], **35**, 1143.
Coffignier, "Manila Copals," etc. *Bull. Soc. Chim.*, 1907 [4], **3**, 453.
Tschirch and Engels, "Congo and Benguela Copals." *Archiv. Pharm.*, 1908, **246**, 293–305.
R. A. Worstall. *J. Amer. Chem. Soc.*, 1903, **25**, 860.

values, respectively, for the white variety, and 30.5 and 89.2 for the same constants of the red variety. The iodine absorption of the white Angola copal was 44.9 and 34.8 for the red variety. Hirschsohn gives 91 as the saponification value of unmelted Zanzibar copal, the melted resin having a value as low as 35.7. For Angola copal he gives 131 to 147.3 for the unmelted and 110.2 to 120.3 for the melted resins.

Kahan (*Arch. Pharm.*, 1910, **248**, 443) gives the following characters for Benin copal:

M. p. .......................................... 120° to 166°
Acid value. ..................................... 101.0
Saponification value. ........................... 149.8
Iodine value. ................................... 61.0

Willner (*Arch. Pharm.*, 1910, **248**, 265 and 285) has examined Loanga and Sierra Leone copals and finds them to have the following characters:

| | Loanga | Sierra Leone |
|---|---|---|
| Soluble in ether-alcohol. .................. | 98.7% | 92.9% |
| Acid value. .............................. | 106 to 115 | 109 to 114 |
| Saponification value. ..................... | 126 to 134 | 146 to 150 |

According to Richmond (*Philippine J. Sci.*, 1910, **5**, 177) Manila copal has an acid value of 128 and saponification value 178. He states that it consists essentially of free amorphous acids, a volatile hydrocarbon, an unsaponifiable resin and a substance which is probably a lactone. The free acids are stated to have the formula $C_{10}H_{15}O_2$, $C_{22}H_{34}O_4$ and $C_{32}H_{50}O_4$.

A number of copals obtained from British West Africa have been examined in the laboratory of the Imperial Institute (*Bull. Imperial Inst.*, 1908, **6**, 245) and the following values recorded.

| | Acid value | M. p. |
|---|---|---|
| Ashanti. ................................. | 124 | 180° |
| Ashanti. ................................. | 134 | 145° |
| Ashanti. ................................. | 133 | 120° |
| Ashanti. ................................. | 126 | 128° |
| Sekondi. ................................. | 133 | 140°–150° |
| Sekondi. ................................. | 133 | 140°–150° |
| Nigeria. ................................. | 110 | 180° |

**Anime resin** is of somewhat variable and, in many cases, doubtful origin.   It apears, in general, to be closely related to elemi and copal, and is usually the product of species of *Bursera*.   Anime is frequently known in English commerce as *soft copal*, whilst Madagascar copal is known in France as *anime*.   The so-called East and West Indian anime is the product of *Hymenæa coubaril*, and the same name has been applied to resins from various other sources.

The chemistry of anime resin is naturally but little understood. Anime appears to contain a large amount of essential oil, which, according to Paoli, is sometimes present to the extent of 24%.

A sample of anime examined by E. Dieterich contained 54.3% of resin soluble in cold alcohol, and 43% of resin soluble in hot (but insoluble in cold) alcohol.

The analytical figures which have been recorded for this resin will be found in the table at the commencement of this section.

## SANDARAC

**Occurrence.**—This resin is the natural exudation from *Callitris quadrivalvis* (*Coniferæ*) and allied species.   Occasionally Australian sandarac, known as "pine-gum" or white pine resin," is found on the market.

**Chemical Composition.**—A. Tschirch and M. Wolff (*Archiv. Pharm.*, 1906, **244,** 684) have found that when sandarac is submitted to Tschirch's systematic scheme for the examination of the resins it yields sandaracinic acid, $C_{22}H_{34}O_5$, which softens at 180° and melts at 186° to 188°; sandaracinolic acid, $C_{24}H_{36}O_3$, which has no sharp m. p., but fuses from 265° to 275°; sandaracopimaric acid, $C_{22}H_{30}O_2$ (identical with Henry's *i*-pimaric acid) which is crystalline and forms flattened rosettes, m. p. about 170°; and a resene, sandaraco-resene, $C_{22}H_{36}O_2$.   In addition to these resins and volatile oils, sandarac contains a bitter principle.

According to Henry, the essential oil contains dextro-pinene and a diterpene boiling at 265°.

**Uses.**—This resin is an important constituent of many spirit varnishes, *e. g.*, label varnishes, negative varnishes, etc.

**Adulterants.**—Sandarac is sometimes adulterated with colophony, and at times with some varieties of cheap dammar.

**General Properties.**—This resin generally occurs in the form of grains varying from 0.5 to 1.5 cm. in diameter; it is also found in short

cylindrical pieces at times agglomerated together, while the finest varieties consist of clear yellow drops. The surface of the grains has a dusty appearance. This resin is somewhat harder than mastic; when chewed it does not agglomerate.

**Specific Gravity.**—This value varies between 1.05 and 1.092.

**Melting Point.**—Sandarac liquefies at 160°.

**Solubility.**—Sandarac is soluble in alcohol, ether, amyl alcohol, acetone, and in several ethereal oils. Chloroform, turpentine, and fatty oils dissolve it partly; in benzene, carbon disulphide, and petroleum spirit it is difficultly soluble, whilst glacial acetic acid hardly affects it. Hirschsohn found from 7 to 8% of sandarac to be soluble in petroleum spirit, and Mauch states that about 5% is soluble in 60% chloral hydrate solution.

**Analytical Data.**—The acid value is of importance in the examination of this resin, and K. Dieterich has suggested the following indirect method for its estimation.

**Acid Value (Indirect).**—1 grm. of sandarac is suffused with 20 c.c. of N/2 alcoholic potassium hydroxide and 50 c.c. of benzin (sp. gr. 0.700), and left to stand for 24 hours in a tightly closed vessel, at the end of which time the contents are titrated back with N/2 sulphuric acid, without the addition of water. The c.c. of standard KOH combined multiplied by 28.02 gives the acid value.

The following analytical characters have been recorded:

| Observers | Moisture, % | Ash, % | Acid number | Acetylated resin | |
|---|---|---|---|---|---|
| | | | | Acid number | Ester number |
| E. Dieterich | | | 97 to 123 | | |
| K. Dieterich | | | 90 to 110 | 166 to 170 | 74 to 82 |
| A. Kremel | | | 144 | | |
| Von Schmidt and Erban | | | 140 | 140 | |
| R. Williams | 0.04; 0.17 | 1.9; 1.4 | 154; 146 | | |

## MASTIC

**Occurrence.**—Mastic is the product of *Pistacia lentiscus*, one of the Anacardiaceæ.

**Commercial Varieties.**—Chios mastic is the kind most generally used and the most prized variety; East Indian or Bombay mastic is also known in commerce.

**Chemical Composition.**—The chemistry of mastic is very little understood, but Flückiger isolated from it 2% of an essential oil,

which consisted chiefly of a slightly dextrorotatory terpene. Tschirch and Reutter (*Arch. Pharm.*, 1904, **242**, 104) found Chios mastic (acid value 59 and saponification value 82.5) to contain: α- and β-masticic acids, 4%; masticolic acid, 0.5%; masticonic aids, α 20%, β 18%; mastico-resenes, α 30%, β 20%; essential oil, 2%; bitter-substance, impurities, etc., 5.5%.

**Uses.**—This resin finds some application in lithographic work. The extreme paleness of the varnish makes it suitable for coating white metallic objects and pictures.

**Adulterants.**—Mastic is sometimes adulterated, especially when in powder, with sandarac, colophony, and other pine resins.

**General Properties.**—The grains of Chios mastic have a long or ovoid shape, varying from 0.5 to 2 cm. in diameter. Bombay mastic sometimes occurs in large irregular pieces, also in the same form as Chios mastic. The grains are always more or less milky, and have a dull appearance due to minute superficial fractures. The colour is yellow or greenish, and the taste and smell remind one of turnips. When chewed, mastic gives a doughy mass; all other resins with which it is likely to be adulterated fall to a powder.

**Specific Gravity.**—Pfaff gives the sp. gr. at 1.04, whilst Schrötter and Brisson give 1.07.

**Melting Point.**—Böttler states that poor-quality mastic softens at 85° to 93°, and melts at 103°, whilst the better qualities soften at 99° and melt at 108°. Johnson gives the m. p. at 100°, whereas Schrötter states that it softens at 80° and melts with partial decomposition between 105° and 120°.

**Solubility.**—Mastic is completely soluble in 80% chloral hydrate solution, and, according to von Schmidt and Erban, is partially soluble in alcohol, methyl alcohol, acetone, acetic acid, chloroform, and oil of turpentine; slightly soluble in carbon disulphide; completely soluble in ether, amyl alcohol, and benzene, and insoluble in petroleum spirit. Chios mastic is soluble to 75% in benzine sp. gr. 0.700, whereas the Indian variety is only soluble to the extent of 10%. Indian mastic when dissolved in turpentine gives a varnish which hardens extremely slowly, whereas a quick drying varnish is obtained from Chios mastic.

**Analytical Data.**—The following figures have been recorded for genuine samples of mastic:

| | A. Kremel | R. Williams | Von Schmidt and Erban |
|---|---|---|---|
| Acid value........... | { 61.8; 70.9 <br> { 67.2 (E. Dieterich). | 50.04; 56.0 | 64.0 |
| Ester value.......... | .................... | 23.00; 23.10 | 29.0 |
| Ash, %.............. | .................... | 0.21; 0.14 | ............. |
| Water, %........... | .................... | 0.97; 1.46 | ............. |

The United States Pharmacopœia (8th Rev.) requires for mastic an acid value of not less than 65.

**Detection of Adulterants.**—The high acid value obtained when sandarac, colophony and other pine resins are present as adulterants will indicate the presence of these bodies.

## DAMMAR RESIN

**Occurrence.**—The chief variety of this resin which occurs in commerce is in all probability the product of a variety of *Hopea*, one of the *Dipterocarpeœ;* but other plants are said to have produced much of the resin, such as species of *Vatica, Dryobalanops, Doona*, and *Vateria*.

**Commercial Varieties.**—The East Indian dammars, obtained from Java, Singapore, and Padang, are the only kinds which are of importance for the European markets; besides these white dammars, there are several descriptions of dark and black resins collected in India, but these varieties are not used commercially in Europe.

**Chemical Composition.**—The constituents of dammar resin which have so far been identified (G. Glimman, *Archiv Pharm.*, 1896, **234**, 584) are as follows: dammarolic acid, $C_{54}H_{77}O_3(COOH)_2$, which is present to the extent of 23%; α-dammarresene, $C_{11}H_{17}O$ (40%, soluble in alcohol); β-dammarresene, $C_{31}H_{52}O$ (22.5%, insoluble in alcohol); ethereal oil and a bitter substance, 0.5%; water, 2.5%; ash, 3.5%; and undefined impurities, 8%.

B. Graf (*Archiv Pharm.*, 1889, **227**, 97) examined 5 samples of East Indian dammar and found about 1% of a free dibasic acid having the formula $C_{18}H_{88}O_3$. Of the other portion of the resin 40% was insoluble and 60% soluble in alcohol. The soluble portion was described as m.p. 61° and having the formula $C_{20}H_{42}O_2$. The insoluble portion contained oxygen and m. p. 144° to 145°. No hydrocarbon could be detected.

**Uses.**—This resin is extensively used in the varnish industry; the so-called "crystal varnishes" consist chiefly of dammar dissolved in oil of turpentine.

**Adulterants.**—The powdered material is often adulterated with colophony; Kauri copal is also a frequent adulterant.

**General Properties.**—Singapore dammar is found in commerce in the form of nodules varying in size from 0.5 in. to 1.5 in. in diameter, sometimes larger, covered with a powdery crust. The material is usually clear and transparent. It is either colourless or at most a faint straw tint. It is friable and breaks easily with a powdery fracture. Batavian dammar has the highest commercial value on account of its perfect colour and the fact that it does not yield a milky solution when dissolved in turpentine.

**Specific gravity** varies from 1.062 to 1.123.

**Melting Point.**—The resin softens at 75° because syrupy at 100° and at 150° is clear and thin. When subjected to destructive distillation dammar resin yields an oil.

**The essential oil of dammar resin** has a golden-yellow colour and a bitter taste. According to H. Haensel, it has a sp. gr. at 21° of 0.9552. It is optically inactive and boils between 205° and 265°. 60% of the oil distils below 240°, this fraction having a sp. gr. of 0.9175. It is soluble in most organic solvents.

**Solubility.**—Dammar is partly soluble in methyl and ethyl alcohols, ether, acetone, and glacial acetic acid. The Batavian dammars dissolve more readily than the other varieties. Benzol, chloroform, carbon disulphide, and oil of turpentine dissolve the resin completely. R. Hirschsohn has examined a large number of samples of dammar and found that, with the exception of *Dammar marmoratus*, all the specimens yielded from 73 to 80% of extract to petroleum spirit, and from 57 to 87% to alcohol of 85% strength. 80% chloral hydrate solution causes the dammar to swell, but only a very small quantity is dissolved after months of standing.

Nine samples of dammar resin obtained from the Federated Malay States have been examined at the Imperial Institute of Great Britain with the following results:

| | M. P. | ASH | ACID VALUE | ESTER VALUE |
|---|---|---|---|---|
| 1. | 90° | 0.26% | 45.3 | 1.4 |
| 2. | 94° | 0.08% | 72 | 0 |
| 3. | 87° | 0.05% | 38.5 | 0 |
| 4. | 180° | 0.52% | 33 | 1.3 |
| 5. | 185° | 0.03% | 72 | 0 |
| 6. | 92° | 0.06% | 33 | 0 |
| 7. | 200° | 0.04% | 46.5 | 0.2 |
| 8. | 97° | 0.25% | 38.5 | 0 |
| 9 | 190° | 0.09% | 55 | 0 |

A sample of dammar resin known as "rock dammar" from Burma has been examined and found to be properly classified amongst the best grades of dammar resin. This so called rock dammar had the following characters:

Ash........................................ 0.55 to 0.68%
Saponification value........................... 31 to 37.1
Acid value................................... 31 to 31.5
Ester value.................................. 0 to 5.6
M. p....................................... 90° to 115°
Sp. gr..................................... 0.980 to 1.013

Gottlieb (*Arch. Pharm.* 1911, **294,** 701) has described two types of dammar obtained from Mid-Borneo. One of these is known as "dammar daging" and is, possibly, identical with rock dammar. It is obtained from *Retinodendron rassak*. It occurs in the form of bright yellow pieces, with a reddish tinge. It consists almost entirely of resin acids with a small amount of resenes. Its characters, are as follows:

Initial melting point............................... 130°
Complete melting point............................ 150°
Acid value...................................... 140–151
Saponification value.............................. 159–165
Soluble in alcohol................................ 82%
Soluble in petroleum spirit........................ 30%
Soluble in carbon disulphide...................... 45%
Soluble in benzene............................... 25%

Coffignier (*Bull. Soc. Chim.* 1911, **9,** 549) gives the following figures for commercial dammar resins.

| Variety | Sp. gr. at 18° | M. p. | Acid value | Sap. value | Insoluble in | | |
|---|---|---|---|---|---|---|---|
| | | | | | Alcohol | Ether | Acetone |
| Padang............. | 1.036 | 95° | 31.4 | 33.7 | 20.3% | 4.5% | 14.7% |
| Borneo............. | 1.048 | 120° | 35.1 | 64.5 | 23.6 | 9.6 | 20.4 |
| Singapore.......... | 1.057 | 95° | 30.1 | 39.3 | 19.1 | 1.0 | 14.0 |
| Pontianac.......... | 1.025 | 110° | 19.9 | 30.9 | 22.4 | 4.1 | 16.4 |
| Sumatra............ | 1.004 | 190° | 59.6 | 64.5 | 45.5 | 37.9 | 45.3 |
| Batjan............. | 1.032 | 105° | 18.5 | 19.6 | 32.8 | 3.2 | 21.3 |

According to S. Stewart (*J. Soc. chem. Ind.*, 1909, **28,** 348), dammar resin may be detected in kauri resin in the following manner. An ethereal or chloroformic solution of kauri resin is not precipitated by alcohol, whereas that of dammar yields a curdy white precipitate. He proposes to extract the sample in a Soxhlet apparatus with absolute alcohol. In the case of kauri resin only vegetable débris and mineral matters are left, but if dammar be present a large

amount of chloroform-soluble resin is left undissolved, averaging about 36%. A fair approximation to the amount of dammar present in kauri resin can thus be obtained.

**Acid Value.**—K. Dieterich has shown that with this resin the direct estimation of the acid value gives low results, so he has proposed the following empirical method for its indirect valuation.

1 grm. of dammar is suffused with 50 c.c. of petroleum spirit, sp. gr. 0.700, 20 c.c. of N/2 alcoholic potassium hydroxide is then added. The whole is allowed to stand 24 hours and is then titrated with N/2 sulphuric acid and phenolphthalein without the addition of water. The acid value (indirect) is the product of the c.c. of KOH multiplied by 28.02.

K. Dieterich has given 20 to 30 as the limit figures (indirect) for this constant.

**Detection of Adulterants.**—E. Hirschsohn (*Zeit. anal. Chem.*, 1898, **37**, 456) states that 5% of colophony can be detected in dammar resin by digesting the sample for half an hour with solution of ammonia (sp. gr. 0.960) and acidifying the filtered liquid with acetic acid. In the presence of colophony, a precipitate of resin acids is formed, whereas pure dammar yields a faint opalescence, since only traces of the acid of dammar resin are extracted by ammonia. The comparative insolubility of dammar in 80% chloral hydrate differentiates it from the conifer resins and softer copals, which are soluble in this medium.

An acid value (indirect) higher than 30 would point to the presence of colophony as an adulterant.

## DRAGON'S BLOOD

The chief variety of dragon's blood is the "Palm dragon's blood," from *Dæmonorops draco*.

**Commercial Varieties.**—The resin obtained from Sumatra or Borneo is the only one of commercial importance. K. Dieterich (*Helfenberger Annalen*, 1903) has investigated the resin obtained from Socotra and from the Canary Islands, but these resins have no technical importance.

**Chemical Composition.**—Tschirch and K. Dieterich found in the resin from *Dæmonorops draco* about 18% of insoluble plant sub-

stances; 2.5% of *dracoalban*, $C_{20}H_{40}O_4$, obtained by the addition of alcohol to the ethereal solution of the sample; about 14% of *dracoresene*, $C_{20}H_{44}O_2$; and a red amorphorus powder, which after purification melts at 72°, obtained by evaporating the filtrate from the dracoalban to dryness and extracting the residue with petroleum spirit. This last substance appears to be a mixture of the benzoic and bezoyl-acetic esters of an alcohol, *dracoresinotannol*, $C_8H_{10}O_2$. Socotra Dragon's Blood, from *Dracæna cinnabari*, a variety not used to any considerable extent, appears to contain esters of both benzoic and cinnamic acids, but no dracoalban.

**Uses.**—This resin is used in the preparation of red spirit varnish. It is one of the best colouring matters that can be employed for this purpose.

**Adulterants.**—Colophony is employed in adulterating the lump dragon's blood. In addition to colophony, oxide of iron, Armenian bole and various gums are said to have been used.

**General Properties.**—This resin is sold in the form of roughly cylindrical sticks about 13 to 14 in. long and about 0.75 in. to 1 in. thick; smaller pieces are not uncommon. It is also sold in the form of balls the size of olives. This is the best variety. A second quality is sold in plates, and a third quality in large pieces. This resin shows various colours according to the quality. The surface is blackish-brown with a deep red fracture. The qualities of lesser value have a deep sealing-wax red appearance. All varieties are opaque, have a sweet taste, and the resin portion falls to a powder when the material is chewed. A good quality dragon's blood must be clear, and when crushed a carmine-coloured powder should be obtained, which dissolves in spirit with a deep red colour. When dissolved in alcohol a good-quality resin only leaves a residue of about 9%, principally vegetable fibre and sand. The less valuable varieties often give 20% of residue.

**Specific Gravity.**—The finer qualities of resin have a sp. gr. of 1.2; the less valuable varieties slightly under this figure.

**Solubility.**—In alcohol and ether this gum is readily soluble, whereas it is only partially dissolved by chloroform, ethyl acetate, petroleum spirit, and carbon disulphide.

**Identification and Analytical Data.**—The following test for distinguishing palm dragon's blood from other varieties has been proposed by K. Dieterich (*Analysis of Resins*, etc., page 154); 10

grm. of powdered dragon's blood should be extracted with 50 c.c. of hot ether, filtered from woody fibre and other insoluble matter, the solution concentrated to about 30 c.c., and the whole then poured into 50 c.c. of cold absolute alcohol. After standing for 1 hour, a white flocculent precipitate of dracoalban, soluble in most organic solvents, but insoluble in alcohol, will be formed if palm dragon's blood be present. Other varieties of the resin are said not to contain this resene. A sample of palm dragon's blood adulterated with colophony, etc., will only respond very slowly to this test.

Gregor and Bamberger found the methoxyl values of three samples of dragon's blood to be 27.6, 25.3, and 33.8. R. Williams found a good commercial sample to contain 9.34% of water and 3.6% of ash. K. Dieterich found 8.3% of ash. The acetyl value of palm dragon's blood was found by K. Dieterich to be about 140.

**Detection of Adulterants.**—Artificial dragon's blood, consisting of colophony mixed with sealing wax, red ochre, and a small quantity of real dragon's blood, when crushed, gives a dull red, not a bright red, powder. When heated it emits an odour similar to that of colophony.

## GUAIACUM

**Occurrence.**—This resin is obtained from the stem of *Guaiacum officinale* and *G. sanctum* of tropical America.

**Chemical Composition.**—According to Döbner and Lücker (*Archiv Pharm.*, 1896, **234**, 590), guaiacum contains about 11% of *guaiaretic acid*, $C_{20}H_{23}O_3(OH)$, crystallising in white lustrous laminæ, m. p. 86°; 70% of $\alpha$- and $\beta$-guaiconic acids, $C_{20}H_{22}O_3(OH)_2$, *guaiacic acid*,[1] $C_{21}H_{19}O_4(OH)_3$ (the $\beta$-resin of Hadelich), insoluble in ether; a yellow crystalline substance, "guaiacum yellow," $C_{20}H_{20}O_7$, m. p. 115°, and soluble in strong sulphuric acid with deep blue coloration; about 10% of gum; 2% of ash; and undefined matters and loss.

[1] The chemistry of guaiacum is of especial interest on account of the synthetic experiments of Döbner, who succeeded in obtaining resin acids closely resembling those of guaiacum. By the condensation of tiglic aldehyde, guaiacol, and cresol, Döbner obtained a brown resin having the composition $C_{30}H_{34}O_4$, which is therefore isomeric with guaiaretic acid. From a study of the reaction in which it is formed, the constitution of the synthetic product is stated to be:

$$CH(CH_3):C(CH_3).CH[C_6H_3.(CH_3)(OCH_3).OH].C_6H_3(OCH_3).OH.$$

In a similar way, by condensing tiglic aldehyde with guaiacol and the dimethyl ether of pyrogallol, an acid isomeric with guaiaconic acid was obtained, and by using only tiglic aldehyde and the dimethyl ether of pyrogallol, an acid having the formula $C_{31}H_{38}O_4$ was obtained. These results have strengthened the hypothesis that many of the resins are formed in nature by the condensation of substances of aldehydic and phenolic character rather than by the oxidation of terpenes.

**Uses and Adulterants.**—Guaiacum is used to a considerable extent in medicines. The mass variety varies greatly in quality, and the commoner kinds frequently contain a considerable quantity of woody fibre. Apart from this impurity which may be regarded as an adulteration, when present in excessive amount, guaiacum sometimes contains an admixture of colophony, and it is also said to be mixed abroad with another speeies of resin unknown in commerce.

**General Properties.**—Guaiacum occurs in rounded tears and in masses of a green or brownish-green colour. It is a glassy, brittle solid, having a somewhat reddish fracture when fresh, but which darkens to green. Its odour and taste are very slight, but on chewing the resin a burning sensation is imparted to the throat. Guaiacum melts at about 85°.

**Solubility.**—Rabenau found from 54 to 74% of guaiacum to be soluble in ether. Very small quantities of guaiacum are soluble in petroleum spirit, up to about 4.0%, after drying the residue at 120°.

**Identification and Analytical Data.**—Numerous oxidising agents produce a blue colour when brought into contact with tincture of guaiacum, and this property is the basis of several useful reactions, as, for instance, in detecting the presence of blood (Vol. VIII) lasted. The coloration is due to the action of oxygen upon guaiaconic acid, the resulting compound probably having the formula $C_{20}H_{20}O_6$. Döbner recommends that the pure acid itself, and not the mixture of acids obtained from a tincture of guaiacum, should be used in such tests.

The proportion of alcohol-soluble matters and of ash in guaiacum are the most important factors in its examination. Ward found the ash in three samples to range from 3 to 6.8%, the matter soluble in alcohol from 87 to 96%, and the matter souble in water from 3 to 4.7%. John Evans found the matter soluble in alcohol in 6 samples to range from 90.0 to 98.5%, the amount of ash in the insoluble matter being very variable, and ranging from 11.5 to 56.2%.

**Acid Value (Indirect).**—The following special method for the estimation of this value is due to K. Dieterich. 1 grm. of resin is suffused with 10 c.c. of $N/2$ alcoholic potassium hydroxide and 10 c.c. of $N/2$ aqueous potassium hydroxide and left for 24 hours in a flask fitted with a glass stopper. After adding 500 c.c. of water, the liquid is titrated back with $N/2$ sulphuric acid and phenolphthaleïn. The following figures for guaiacum have been recorded:

| Observer | Acid value | After acetylation | |
| --- | --- | --- | --- |
| | | Acid value | Ester value |
| A. Kremel.............. | 23 to 44 | ......................... | ........... |
| K. Dieterich............ | ........... | { Mass variety, 46 to 53<br>{ Purified by ⎱ 13.6 to<br>{ Alcohol ⎰ 13.9 | 122 to 139<br>149 to 150 |

The acid values after acetylation are widely different in the case of the mass variety and of the purified guaiacum but no explanation of the discrepancy is offered by Dieterich. Guaiacum contains mere traces of esters only.

The methoxyl value of guaiacum ranges from 74 to 84 (Gregor and Bamberger).

E. J. Parry has found the following values for purified guaiacum resin that is the resin freed from impurities:

Mineral matter................................. 1–4%
Acid value..................................... 60–70
Soluble in 90% alcohol......................... 87–98%
Acid value of acetylated resin................... not over 50
Ester value of acetylated resin.................. 125–150
Methoxyl value................................. 70–85
Soluble in petroleum spirit...................... not over 2%

**Detection of Adulterants.**—For the detection of colophony in guaiacum, the Storch-Morawski reaction may be employed (see Colophony). Hager states that this adulterant may be detected by adding excess potassium hydroxide solution to an alcoholic solution of guaiacum. An insoluble resin soap will be precipitated in the presence of colophony. The potassium salt of guaiaretic acid is, however, precipitated from guaiacum by this method (Döbner).

Hirschsohn states that the presence of either colophony or of a foreign species of guaiacum, such as the so-called Peruvian guaiacum (*Guaiacum peruvianum odoriferum*), may be detected by adding a solution of bromine to a chloroformic solution of guaiacum. Pure guaiacum yields a blue colour, whilst an adulterated sample will give a red coloration.

## SHELLAC

**Occurrence.**—Shellac is the secretion of the lac insect, *Tachardia lacca* (*Coccidæ*) found on a large number of widely different plants,

such as *Betua frondosa* and *Ficus religiosa,* and on certain other trees specially grown for the insect.

**Commercial Varieties.**—Crude "stick lac" contains much impurity such as dirt and woody fibre, while the crushed and washed lac, known as "seed lac" is correspondingly purer. The purified resin is the form in which most of the lac is sold, and is then known as "shellac." With insignificant exceptions all the "shellac" of commerce is manufactured in or about Calcutta. Some of the shellac of commerce is arsenical, being coloured with a small quantity of orpiment. The bulk of the shellac of commerce is sold on a standard known as ⟨TN⟩. This by custom is allowed to contain up to 3% of rosin which was, apparently, first used to aid the filtration of the lac. Proportional allowances for adulteration over 3% have to be made to buyers. Pure shellac is usually purchased with the specification that it shall be pure.

**Button Lac.**[1]—Button lac, a form in considerable demand for certain purposes, is melted and poured so as to form large, round, flat pieces, which, are of a dark brown to reddish colour. Button lac is sold on standard, and may be pure, or may contain 10, 20 or 30% of rosin according to standard.

**Garnet Lac.**—Garnet lac is made into thick, flat irregular pieces and is allowed by custom of the trade to contain up to 10% of rosin, allowances being made for adulteration above this quantity.

**Chemical Composition.**—The chemistry of shellac has been but incompletely studied, though a few well-defined constituents have been recognised. In addition to accidental impurities, such as water (up to 4%) and small quantities of sand, woody fibre, etc., shellac contains *wax* in proportions varying from traces up to about 6%. There is also usually from 2 to 6% of laccin pigment present, and a small quantity of *laccainic acid,* $C_{16}H_{12}O_8$, which forms an important constituent of lac dye, and is a substance closely allied to the colouring matter of cochineal. The resinous matter constitutes the bulk of shellac and was prepared by A. Tschirch by exhausting crushed shellac under a reflux condenser with petroleum spirit to remove the wax and then repeatedly treating the dried residue with warm water until the liquid was no longer coloured, an additional 6.5% being

[1] Shellac wax melts at 59°, and consists of a mixture of equal parts of free alcohols (chiefly myricyl and ceryl alcohols) and of the stearic, palmitic, and oleic esters of these alcohols (Benedikt and Ulzer).

thus removed. Of the resinous matter thus purified 35% was dissolved by ether, and consisted of traces of higher fatty acids, a yellow colouring matter called *erythrolaccin*, $C_{15}H_{10}O_5 + H_2O$ (apparently a hydroxy-methyl-anthraquinone), a small quantity of a crystalline odoriferous substance, and compounds apparently of the nature of *resenes*. The 65% of shellac resin not dissolved by ether consisted chiefly of the aleuritic ester of a very unstable *resinotannol*. *Aleuritic acid* itself, $C_{13}H_{26}O_4$, crystallises from aqueous alcohol in rhombic leaflets, or from water or chloroform, in needles melting at 101.5°.

The most recent work on the chemistry of shellac is that of Harris and Nagel (*Ber.*, 1922, **55**, [13] 3833). The wax and colouring matter were removed by petroleum spirit and water and the residue extracted with ether. The resin insoluble in ether was then fully investigated. By treatment with normal potassium hydroxide solution at ordinary temperatures, potassium aleuritate is deposited, the amount being 22 to 24 % of the resin used. The filtrate from this salt was rendered acid with dilute sulphuric acid. This filtrate was extracted with ether and a mixture of resin acids obtained. These can be separated to some extent by means of the barium or zinc salts, but the most satisfactory results were obtained by esterifying with methyl alcohol and hydrogen chloride. By this means methyl shelloate $C_{17}H_{24}O_6$, crystallising in long prismatic rods, was obtained. This melts at 149° and has a specific rotation in methyl alcohol of +32.61°. On hydrolysis the free acid is obtained. This is termed shelloic acid, and forms colourless leaflets melting at 199.5° to 201°.

The non-crystalline residue of esters from which the methyl shelloate has been separated consists of compounds of hydroxy-acids. This investigation has rendered it very improbable that shellac is the aleuritic ester of any high alcohol, since no trace of any such alcohol would be detected, whereas if it were present as the constituent of esters represented by the apparent "ester" value of shellac, it would be found in considerable amount.

Since it is established that the resin (*i. e.* the ether-insoluble resin) does not contain a free acid, it appears to be highly probable that the principal part of the resinous matter of shellac is a mixture of hydroxy-acids which are united to one another in the form of lactides or lactones.

When shellac is bleached to form white shellac, a variety used for pale shellac varnishes and polishes, chlorine compounds are almost invariably employed as the bleaching agent. The constituents of the shellac are considerably altered by this somewhat drastic treatment, so that analytical values obtained for normal, unbleached shellac must not be taken to apply to the bleached variety.

The so-called artificial shellacs are merely mixtures of other resins, sometimes natural, sometimes artificial, and often containing a little genuine shellac as their basis.

For attempts to synthesise shellac see Harries and Nagel (*Wiss. Veröff. Siemens-Konz* 1924, **3**, 12).

**Uses.**—Shellac is used very largely in various industries, notably for the preparation of a certain class of polishes and varnishes, and for the stiffening of hats and certain textile materials such as crape. It is also a constituent of sealing-wax, marine glues, and some kinds of cement.

**Adulterants.**—Shellac is an article of considerable value, and its price is frequently very high, hence it is extensively adulterated, the usual admixture being common rosin. Admixture with the quantities referred to above is not regarded as adulteration.

**Solubility.**—Shellac is almost entirely soluble in methyl and ethyl alcohols, acetic acid, alkalies, and solution of borax; only partially soluble in ether, ethyl acetate, chloroform, acetone, and carbon disulphide, and almost insoluble in benzene, toluene and petroleum spirit.

According to Mauch, on treating shellac with an 80% aqueous solution of chloral hydrate it first swells up and then dissolves almost entirely.

It has been pointed out by Ulzer and Defris that shellac resin acids behave quite differently from the resin acids of colophony in Gladding's or Twitchell's process, and that the former appear to be more nearly related to the fatty acids than to the resin acids of colophony. (See *J. Soc. Chem. Ind.*, 1897, **16**, 364.)

On treating shellac previously dried at 120° with petroleum spirit, Hirschsohn found from 0.4 to 6.3% to pass into solution. These figures probably represent a portion of the wax present in the samples examined.

The ready solubility of shellac in hot aqueous solutions of potassium and sodium carbonates, alkali hydroxides, and borax is well

well known, and this property is utilised in several ways. On the one hand, it is made use of in the preparation of the so-called water varnishes employed in the finishing of leather and, on the other hand, for the production of bleached shellac and of shellac soluble to a clear solution in alcohol. The shellac remains unchanged in these alkaline solutions and dries to a hard coat. It can be precipitated from the solution by an acid.

Benedict and Erlich have observed that shellac is largely converted by dilute alkalies into a balsam-like mass, described by them as "*liquid shellac.*" This is prepared by boiling 10 parts of shellac (previously freed from wax) with a solution of 3 parts of sodium hydroxide in 20 of water, acidifying the cooled mass with sulphuric acid, and extracting with ether. The ether is distilled, the residue (amounting to about 70% of the wax-free resin) consisting of the "liquid shellac." The product is probably little more than shellac resin hydrolysed, and containing a considerable proportion of water (Parry). By mixing liquid and ordinary shellac, plastic masses of any degree of softness can be obtained.

*The Analysis of Shellac.*—Prior to 1901, the analysis of shellac was on a most unsatisfactory basis, and nearly every figure published was unreliable, as the results had been obtained on commercial samples containing variable quantities of rosin. In a series of papers E. J. Parry (*Chemist & Druggist*, 1901, 2, 689; 1902, 670; 1903, 1, 175; and 1905, 556), working with shellac, prepared from stick lac by himself, and therefore of absolute purity, published numerous figures which have been amply confirmed by the examination of thousands of samples subsequently, and which are now the accepted figures for shellac analysis.

For detecting rosin in shellac, the Storch-Morawski reaction gives a useful indication, using sulphuric acid of specific gravity 1.5 on a solution of the shellac in acetic anhydride. Parry however prefers the following test. The copper salts of rosin acids are intensely green in colour and are soluble in petroleum spirit, which is not the case with the acids of shellac. But as a small amount of rosin in shellac is so "protected" by the large amount of shellac, it is almost impossible to dissolve much of the rosin out in a reasonable time unless the sample be in a very fine state of division. If therefore the sample be dissolved in a little warm alcohol and the alcoholic solution poured into water, the mixed resins are precipitated in a very

fine state. This precipitate is collected and dried with blotting paper and finally in a dessicator when it forms a nearly impalpable powder. It is then shaken or rubbed with petroleum spirit, and the filtrate is shaken with a very dilute solution of copper acetate. In the presence of very small quantities of rosin the petroleum spirit assumes a vivid green colour.

As a quantitative method the iodine absorption value is the only practicable method for the valuation of shellac. This was established by Parry (*loc. cit.*), who gives the following figures on a number of typical samples, by the Hübl method

| | | | |
|---|---|---|---|
| Button lac (origin known) | 7.8 | Orange lac (origin known) | 9.4 |
| Button lac (origin known) | 8.6 | Orange lac (origin known) | 10.0 |
| Button lac (origin known) | 7.9 | Orange lac (origin known) | 8.0 |
| Button lac (origin known) | 7.5 | Orange lac (origin known) | 10.2 |
| Button lac (origin known) | 8.7 | Orange lac (origin known) | 8.1 |
| Orange lac (origin known) | 9.6 | Orange lac (origin known) | 10.1 |
| Orange lac (origin known) | 8.0 | Orange lac (origin known) | 7.6 |
| Orange lac (origin known) | 11.0 | Orange lac (origin known) | 8.9 |
| Orange lac (origin known) | 9.1 | | |

These figures were confirmed by the examination of a number of samples of lac stripped from the original twigs, in which the iodine value was found to be 7.3 to 8.6, and also by the examination of the samples of seed lac from various districts, the values varying from 7.9 to 11.0.

The average iodine value for rosin, as determined by the Hübl method is 125, so that if 10 be taken for shellac and 125 for rosin the amount will not be far from the truth.

A number of mixtures of known composition were prepared and the calculated results compared with the actual quantities present. These were as follows:

| ACTUAL | FOUND | ACTUAL | FOUND |
|---|---|---|---|
| 13.5% | 12.9% | 11.5% | 8.3% |
| 22.4 | 20 | 5.9 | 4.4 |
| 22.5 | 20.4 | 17.6 | 17.5 |
| 37.3 | 36.4 | 52.6 | 48.2 |
| 18.0 | 16.1 | 25.4 | 22.8 |
| 33.5 | 35.4 | 26.5 | 25.6 |
| 31.8 | 29.4 | 15.4 | 13.8 |

The standard method of analysis of shellac governing English contracts is that based on the iodine absorption as estimated by the Hübl method. The official method of the United States Shellac Importers Association is also based on the iodine value, but

the Wijs method is used in this process, as suggested by Langmuir (*J. Soc. Chem. Ind.*, 1905, **24,** 12).

As the figures obtained by the Wijs process are entirely different for both shellac and for rosin, different values are obtained, and as the Wijs process is exceedingly sensitive to minute variations in conditions with resinous substances, the most minute details of procedure have to be laid down. These will be dealt with later.

The treatment of shellac with alcohol and hydrochloric acid for the purpose of separating the oxy-acids has been recommended by H. Endemann (*Zeit. angew. Chem.*, 1907, **20,** 1776) for the valuation of commercial shellac.

2 grm. of the finely powdered sample are mixed with 4 grm. of very fine washed sand. 4 c.c. of alcohol and after a time 200 c.c. of concentrated hydrochloric acid are added. The mixture is stirred and evaporated to dryness on the water-bath. Alcohol and hydrochloric acid are again added to the residue, and the evaporation is repeated. After the contents of the basin have been heated in an air-bath for 2 hours at a temperature of 105°, the residue, when cold, is first moistened with a small quantity of hydrochloric acid, then with 20 c.c. of alcohol, and allowed to stand overnight. The solution is then poured through a filter and the filtrate is collected in a weighed flask and the residue is washed with successive quantities of alcohol until the filtrate measures about 150 c.c. The insoluble portion consists of wax, myricyl alcohol, and condensed oxy-acids; it always retains chlorine and is unsuitable for weighing. The alcoholic filtrate is evaporated, and the residue is weighed after drying for 2 hours at a temperature of 102°. All acid compounds which do not belong of the oxyacids are thus obtained. The best commercial shellacs contain about 87% of oxy-acids, 5% of wax, and 8% of soluble fat and resin, besides inorganic salts. If more than 8% of fat and resin be obtained, the sample is either adulterated or inferior in quality. The results of the analysis can be expressed in terms of soluble resins above 8%.

**The Acid and Ester Values of Shellac.**—K. Dieterich made many experiments with mixtures of shellac and colophony and finally came to the conclusion that these values cannot be usefully employed in shellac analysis.

Parry (*loc. cit.*) has made a number of estimations of the acid and ester value of shellac, and considers these figures useful

checks in examining shellac samples. The average acid value for pure shellac is 60, whilst for rosin it is about 165. The ester value for pure shellac is about 150, whilst for rosin it is not above 6. It is bad to use excess of alkali and titrate back with acid, on account of the dark colour of the solutions.

The following process for the estimation of colophony in shellac based on the method of Gladding and Twitchell for the separation of fatty and resin acids is recommended E. J. Parry. This method only gives good results when more than 20% of the colophony is present. About 0.5 grm. of the sample is dissolved in the smallest possible quantity of alcohol and the solution cautiously treated with alcoholic potassium hydroxide till it is just neutral to phenolphthaleïn. This solution, containing the potassium salts of the shellac and resin acids, together with the neutral constituents of the shellac, is poured into about 100 c.c. of water contained in a separator, and about 0.5 grm. of silver nitrate, dissolved in a little water, added. The acids are precipitated as silver salts, and on shaking the liquid twice with ether, the silver salts of the resin acids of colophony are completely dissolved, while the silver compounds of the shellac acids remain insoluble. The ethereal solution is filtered, repeatedly agitated with water to remove silver nitrate, dilute hydrochloric acid added, and the liquid well shaken. The silver salts are decomposed, silver chloride being precipitated, and the resin acids recovered by evaporating the washed ethereal solution to dryness. The purity of the resin acids thus obtained may be verified by their iodine absorption. The above process only gives approximate results, the chief source of error being the slight solubility of a portion of the neutral constituents of shellac in ether, so that the results are rather higher than the truth.

**White or bleached shellac** occurs in twisted masses resembling "peppermint rock." It contains aleuritic acid, but no wax. It is prepared by dissolving ordinary shellac in an alkaline solution, preferably sodium carbonate, and treating the liquid with chlorinated lime. Hydrochloric or sulphuric acid is then added, when the shellac is precipitated in a nearly colourless condition. The bleaching is due to the destruction or alteration of the erythrolaccin. Bleached shellac, even when quite hard, usually contains a considerable proportion of water. It is not entirely soluble in alcohol, a substance resembling "lackstoff" being left as a residue. It is

said to lose its solubility in alcohol very greatly by keeping, unless it is stored under water. In epichlorhydrin, bleached shellac is but sparingly soluble, and not much more so when the liquid is warmed; but in warm dichlorhydrin it is almost completely soluble. According to Tschirch, bleached shellac contains chlorine, so that the iodine absorption is materially modified.

**The American Standard Method of Analysis.**—Owing to the fact that London is the principal centre of the shellac trade, and enormous quantities are sold from London to the United States, and that contracts made in the United States are controlled by a detailed method of analysis, it is necessary to give in detail the method as adopted by the United States Shellac Importers Association. This is as follows:

**Estimation of Rosin.**—*Solutions Required.*—Iodine monochloride solution containing 13 grm. of resublimed iodine per litre of glacial acetic acid. The acid must have a melting point of 14.8° C., a strength of exactly 99% and must be free from reducing impurities as shown by its action on dichromate in sulphuric acid. If these specifications are not fulfilled the results of the rosin estimation will be erratic. The solution is best made by dissolving 13 grm. of iodine in a litre of the above acid, using gentle heat if necessary and estimating its strength by titration with thiosulphate. Set aside 50 to 100 c.c. of this solution, and introduce dry chlorine gas into the remainder until the characteristic colour change occurs, and the halogen content has been doubled. Then by titration ascertain if the halogen content has been more than doubled, and if so, reduce it by adding the requisite quantity of the iodine acetic acid solution. A slight excess of iodine does no harm, but an excess of chlorine must be avoided.

*Acetic Acid.*—99% glacial acetic acid of the specifications given above.

*Chloroform.*—Pure chloroform.

*Sodium Thiosulphate Solution.*—Dissolve 24.83 grm. of pure salt in a litre of cold, boiled, distilled water. Standardise by titrating against freshly sublimed iodine. It is recommended that the resublimed iodine be collected into a glass stoppered weighing bottle, and weighed after cooling.

*Starch Solution.*—0.2 grm. in 100 c.c. of boiling water.

The analysis is performed by introducing 0.2 grm. of the ground shellac into a 250 c.c. stoppered bottle, adding 20 c.c. of glacial

acetic acid, and warming until solution is complete (except for the small amount of wax present).   Ten c.c. of chloroform are added and the liquid cooled to 22°.   The bottle should be allowed to stand half immersed in water at 22° for half an hour and then 20 c.c. of the Wijs solution added.   The mixture is to be kept at 22° for 1 hour.

At the end of one hour, add 10 c.c. of 10% potassium iodide solution, washing down any iodine from the stopper into the bottle. The liquid is now titrated with the thiosulphate solution, until it becomes of a pale straw colour.   15 c.c. of starch solution is added and the titration is completed.   The intense importance of observing these detailed conditions is emphasised by the advice that "a standard sample of known iodine value can be procured from the United States Shellac Importers Association's Secretary for the nominal fee of one dollar" and operators are advised to use such a sample as a check, on any set of tests made on unknown samples.   In the case of grossly adulterated samples, or in the testing of pure rosin, from 0.1 to 0.15 grm. of the sample should be used.   Under the above conditions it is claimed that no pure shellac shows a higher iodine absorption than 18.   With this conclusion the present writer disagrees, and the use of this figure renders pure fine orange shellacs liable to condemnation as adulterated.

It is also claimed that the iodine value of bleached shellac is 10 but this, obviously, varies with the details of bleaching.

The iodine value of rosin is taken as 228, and from the values 18 and 228, the percentage of adulteration is calculated.   In estimating the iodine value of shellac and rosin by the Hübl method, it is quite sufficient to specify that method without a mass of detail, and minute variations in conditions are practically without effect on the result.   From this point of view the Hübl method appears to be the more useful of the two.

## OLEO-RESINS.  BALSAMS

The *oleo-resins* are a class of resinous exudations from plants, excreted naturally or obtained by tapping the trees.   They consist essentially of mixtures of resins and volatile oils.

The term balsam has a somewhat loose application.   The word is more particularly applied to such of the oleo-resinous exudations

of plants as contain benzoic or cinnamic acid and yield cinnamate or benzoate of methyl or ethyl on distillation. They are more or less viscous, and yield essential oils on distillation with water. The term balsam is also applied to such materials as "Canada balsam" and "copaiba balsam," which are oleo-resins not containing or yielding benzoic or cinnamic acid. The oleo-resins are not sensibly soluble in water, though some yield traces of formic and probably succinic acid to that solvent and, according to Tschirch, an alkaloidal substance.

### Common Turpentine

Common or American turpentine is the oleo-resin collected from pine-trees growing in the Carolinas and other of the southern United States. The greater part of American turpentine is obtained from the "longleaf" pine (*Pinus australis*). The "loblolly" or "oldfield" pine (*P. tæda*), the "pitch" pine (*P. rigida*), and the "swamp" or Cuban pine (*P. cubensis*) supply comparatively small quantities only. The crude turpentine is collected in pockets cut in the trees a few feet from the ground. The flow of the first year, called *virgin dip*, is the best, and one barrel yields on distillation about six gallons of essential oil and a residue known as *window-glass rosin*. *Yellow dip*, the product of the second and subsequent years, yields about four gallons of oil per barrel, and furnishes the medium qualities of rosin. The turpentine which hardens on the trees is called *scrapes*. On distillation, it yields about two gallons of oil per barrel and leaves a very dark coloured (nearly black) rosin.

The essential oil obtained by the distillation of American turpentine constitutes the American oil of turpentine of commerce (which see). The resinous residue is known as colophony (page 242).

American turpentine was formerly distilled dry, but now an addition of water is usually made, so that the oil may pass over in a current of steam, and overheating be avoided. The stills, which are of copper, hold from 8 to 50 barrels. The vapour is condensed in a worm surrounded with cold water, the distillate flows into a tank, where the oil collects on the surface. The resin which remains in the still is run off while still fluid and constitutes the common *rosin* or *colophony* of commerce.

### Bordeaux or French Turpentine

This product, also called *Gallipot* or *Barras*, is mostly the product of *Pinus maritima*, but smaller quantities are obtained from the *Pin franc*, or frankincense pine. In physical characters it closely resembles American turpentine, but on distillation yields a lævorotatory oil and a resin which contains *pimaric acid*.

Russian turpentine is the oleo-resinous exudation from the Scotch fir, *Pinus sylvestris;* German, from the same species or from *P. rotundata;* Austrian, from *P. laricio;* Hungarian, from *P. pumilio;* Strassburg or Alsace turpentine is the product of the silver fir, *Pinus picea* or *pectinata* (otherwise, *Abies excelsa*). It has an agreeable odour, resembling that of lemon.

The following analytical data have been recorded for various turpentines.

|  | Acid value | Ester value | Sapon. value |
|---|---|---|---|
| E. Dieterich: |  |  |  |
| American.................... | 112–139 | 9.8–32.5 | 140–161 |
| French....................... | 105–141 | 2.8–9.8 | 109–149 |
| Carpathian (*P. cembra*)......... | 117–119 | 56–60 | 167–179 |
| *P. sylvestris*.................. | 129–145 | 35–39 | 167–180 |
| K. Dieterich: American.......... | 107–116 | 4.1–20 | 115–134 |
| Dietze: French................. | 120–120.4 | 1.8–3.0 | 121–123 |

More constant and reliable results would be obtained by first driving off the essential oil in a current of steam, and estimating the acid and saponification values of the residue, as the variable amount of essential oil consists almost entirely of neutral and unsaponifiable hydrocarbons.

### Venice Turpentine or Larch Turpentine

**Occurrence.**—This product is the oleo-resin from *Larix Europœa* or *Larix decidua*.

**Uses.**—This oleo-resin is largely employed for lithographic purposes, also as an ingredient for certain varnishes.

**Adulterants.**—Common turpentine and artificial products consisting of colophony, rosin oil, and oil of turpentine are often employed.

**General Properties.**—Venice turpentine is a viscous liquid of a yellowish or greenish-yellow colour. Resin acids never crystallise out from this oleo-resin, as is the case with some other turpentines.

It has a characteristic smell and bitter taste, attributed by Flückiger to the presence of a glucosidal principle.

**Solubility.**—This oleo-resin is completely soluble in alcohol, ether, acetone, glacial acetic acid, chloroform, and turpentine, but is only partly dissolved by petroleum spirit.

**Identification.**—L. E. Andés recommends as a useful adjunct to the analytical values and the observation of the odour, inflammability, and solubility in 90% alcohol the following test, suggested by Hirschsohn, who has observed that ordinary turpentine, on treatment with 5 volumes of ammonia solution (sp. gr. 0.96), gradually yields a milky emulsion, while in the case of larch turpentine the liquid remains clear. When the lower layer of larch turpentine is stirred it is gradually transformed into a semi-solid, opaque substance, while the supernatant liquid becomes slightly turbid. Ordinary turpentine, however, is immediately distributed and the milky emulsion rapidly solidifies to a gelatinous mass. In the case of a mixture of the two in equal parts, the substance is distributed throughout the ammonia, and a solid mass, which clears on heating, is obtained in about 5 minutes. When the mixture only contains about 20% of ordinary turpentine, the milky emulsion becomes clear on heating the tube in boiling water, but no solidification occurs. Comparative tests with genuine larch turpentine may serve to detect smaller quantities.

**Analytical Data.**—The following analytical data have been recorded for Venice or larch turpentine:

|                          | Acid value | Ester value | Sapon. value | Iodine value |
|--------------------------|------------|-------------|--------------|--------------|
| A. Kremel                | 68–70      | . . . . . . | . . . . . .  | . . . . . .  |
| Von Schmidt and Erban... | 68         | 30          | 97           | . . . . . .  |
| Von Italie               | 70         | 50          | 120          |              |
| E. Dieterich             | 64–77      | 35–56       | 108–133      | . . . . . .  |
| K. Dieterich             | 67–69      | 46–55       | 115–128      | . . . . . .  |
| A. Rudling               | 74         | 48          | 122          | 148          |

K. Dieterich has also recorded the following acetyl values for larch and ordinary turpentine:

|                            | Larch turpentine | Common turpentine |
|----------------------------|------------------|-------------------|
| Acetyl-acid value          | 70–72            | 124–126           |
| Acetyl-ester value         | 109–119          | 62–94             |
| Acetyl-saponification value| 179–191          | 188–217           |

**Detection of Adulterants.**—*a*. Rosin oil.  To detect rosin oil G. Fabris dissolves 5 grm. of the sample in 20 c.c. of 95% alcohol, and adds a 10% solution of potassium hydroxide till the mixture is alkaline to phenolphthalein.  Venice turpentine thus treated yields a perfectly clear solution, whereas the factitious turpentine containing rosin oil becomes turbid, and on standing oily drops separate.

A factitious article, to which the name "Venice turpentine" is improperly applied, is made by mixing rosin, rosin oil and oil of turpentine.  It is employed in the manufacture of varnish and sealing-wax. · Such an article would necessarily give variable analytical figures, dependent on the proportions of its constituents, but a mixture of the three substances mentioned above would have a high acid value, a very low ester value, and would contain a considerable proportion of unsaponifiable matter.  Six samples examined by G. Fabris gave distillates below 250° varying from 6.5 to 13%; acid values from 105 to 114; and saponification values from 113 to 119.  Genuine larch turpentine is said to yield not less than 15% of essential oil.

A factitious Venice turpentine analysed by A. Rudling had an acid value of 103; a saponification value of 117.6; and an iodine value of 109.8.

A sample of so-called "Venice turpentine" examined in A. H. Allen's laboratory by A. R. Tankard gave the following results: Acid value 80.1; ester value 7.73; saponification value, 87.8; unsaponifiable matter (liquid, and gave reactions of rosin oil), 51.92%; essential oil (volatile with steam), 3.0% and optical activity of 10% alcoholic solution of residual resin, +1.75° per 100 mm.  It will be noticed that these artificial products generally have the acid and saponification values close together.  When steam distilled, oil of turpentine can be detected in the distillate, while a soft, sticky mass left in the distilling flask denotes the presence of rosin oil.  This can be separated after saponification and detected by the usual methods.

*b*. Ordinary turpentine.  Walbaum (*Ark. Pharm. Kemi*, 1908, 105) has suggested the following method for the detection of this adulterant.  10 grm. of the turpentine are dissolved in 30 c.c. of ether; the solution is maintained at a *constant* temperature of 20.5° for 10 minutes.  Then 8 c.c. of N/2 ammonia solution previously brought to the same temperature are added, and the mixture is well

## COMPOSITION OF CONIFEROUS RESINS[1]

| | Strassburg | Bordeaux | Venice | Finland | Jura | Canada | White pitch. (Russian "Beljivar") |
|---|---|---|---|---|---|---|---|
| Botanical origin...... | White fir, *Abies pectinata* | *Pinus maritima.* | Larch, *Larix decidua.* | *Pinus sylvestris.* | *Picea vulgaris.*[2] | *Abies canadensis.* | *Abies picha,* or *Abies sibrica.* |
| **Resin Acids** | | | | | | | |
| A. Soluble in Am. carbonate, amorphous. | Abienic, $C_{15}H_{20}O_2$ (m. p. $114$–$115°$), $K_1$, cold, $9$–$10$ %. | Pimarinic, $C_{14}H_{20}O_2$, $K_1$, hot or cold, $6$–$7$ % | ...... | ...... | Picea-pimarinic, $C_{15}H_{20}O_2$ ($132$–$135°$), $2$–$3$ %, $K_1$, cold and boiling, $I_1$. | Canadinic, $C_{15}H_{20}O_2$ ($135$–$136°$), $13$ %. | Beljabien-imic, $C_{15}H_{20}O_2$, $4$–$5$ %. Belli-abietinic, $C_{20}H_{30}O_2$ (cryst.). ($2.5$–$3$ %). |
| B. Insoluble in Am. carbonate. | | | | | | | |
| *a.* Crystallisable.... | Abietolic, $C_{20}H_{30}O_2$, $145$–$153°$), $K_1$, cold; $K_1$ hot, $1.5$–$2$ %. | Pimaric, $C_{20}H_{30}O_2$ ($144$–$146°$), $15$–$20$ %. | Laricinolic, $C_{20}H_{30}O_2$ ($147$–$148°$), $K_1$, more, with excess $4$–$5$ %. | Silveolic, $C_{15}H_{20}O_2$ ($138°$), $K_1$, cold and hot, $1.5$ %, $I_1$. | Picea-pimaric, $C_{20}H_{30}O_2$ ($144$–$145°$), $K_1$, cold and hot, $I_1$ $1.5$–$2$ %. | Canadolic, $C_{20}H_{30}O_2$ ($143$ $K_1$, cold. (nearly) hot, $3$ %. | ...... |
| *b.* Amorphous...... | Abietinolic, $C_{20}H_{30}O_2$, $46$–$50$ %. | Pimarolic, $C_{20}H_{30}O_2$, $48$–$50$ %. | Larinolic, $C_{20}H_{30}O_2$, $55$–$60$ %. | Silvinolic, $C_{20}H_{30}O_2$, $58$–$60$ %. | Picea-pimar-olic, $C_{20}H_{30}O_2$, $48$–$50$ %. | Canadinolic, $C_{20}H_{30}O_2$, $48$–$50$ %. | Beljabie-tinolic, $C_{20}H_{30}O_2$, $42$–$50$ %. (α & β). |
| α-acid, pptd. by alcoholic lead acetate. | ($95$–$96°$) $K_1$, cold; more with excess. | ($90$–$91°$) $K_1$, cold or hot. | ($80$–$81°$) $K_1$; more with excess. | ($85$–$90°$)$K_1$, $I_1$. | ($90$–$95°$) $K_1$; cold and hot. | ($89$–$95°$). | ...... |
| β-acid, not ppptd. by alcoholic lead acetate. | ($93$–$94°$) $K_1$, cold gradually increasing. | ...... | ($85$–$86°$) $K_1$, more cold, with excess of KOH. | ($89$–$95°$)$K_1$, $I_1$. | ($88$–$94°$) $K_1$, cold and hot $I_1$. | ($90$–$95°$) $K_1$. | ...... |
| **Indifferent Resins.** | | | | | | | |
| Insoluble in alkalies... | Abietoresene $C_{20}H_{30}O$ ($168$–$169°$), $12$–$16$ %. | Bordoresene, viscid, $5$ %. | Resene, indefinite, $14$–$15$ %. | Silvoresene ($58$–$60°$), $20$–$21$ %. | Juroresene, $C_{20}H_{30}O$, $10$–$12$ %. | Canadoresene, $C_{20}H_{30}O$ ($170°$), $1$–$12$ %. | Beljoresene, $C_{20}H_{30}O$, $15$–$18$ %. |

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| | | | | | | | |
|---|---|---|---|---|---|---|---|
| **Essential Oil.** | | | | | | | |
| A. Readily volatile with steam | B. p. 162-163°, 24-25 %. | B. p. 150-175°, 14 %. | B. p. 157°, 15-16 %. | B. p. 155-163°, Sp. gr. .840. 15%. | 32-33 %. | 23-24 % Lævorotatory | B. p. 158-165° dextrorotatory, 20 to 30 %. Sp. gr. 0.863. Sol. in 90% alcohol, 1 : 10. |
| B. Tailings | 4-6 % | 15 % | B. p. 190°, 5-6 %. | | | | Traces. |
| **Minor Constituents.** | | | | | | | |
| Bitter principle, alkaloid, succinic acid, colouring matter, water, and impurities. | 1-2 % | 2-4 % | 1-2 % | 1-2 % | 1-2 % | 1-2 % | |
| **Reference.** | | | | | | | |
| Original | Arch. Pharm., 1900, p. 411. | Arch. Pharm., 1900, p. 630. | Arch. Pharm., 1900, p. 387. | Arch. Pharm., 1901, p. 167. | Arch. Pharm., 1900, p. 616. | Arch. Pharm., 1900, p. 489. | Arch. Pharm., 1902, p. 584. |
| Abst. Jour. Chem. Soc. | 1900, i, 679. | 1901, i, 220. | 1900, i, 680. | 1901, i, 397. | 1901, i, 91. | 1900, i, 678. | 1903, i, 106. |

[1] $K_1$, $K_2$, indicate in this table the formation of a mono- or di-potassium salt, respectively; $I_1$ indicates the formation of a monoiodo-derivative.
[2] The oleo-resin of *Picea vulgaris* grown at Siebenbürgen gave very similar results to the Jura specimen, but the formula of picea-pimarinic acid given as $C_{18}H_{28}O_2$, that of the picea-pimarolic acids a $C_{18}H_{28}O_3$, and that of the resene as $C_{18}H_{28}O$ (*Arch Pharm.*, 1902 240, 272).

agitated. Pure Venice turpentine under these conditions sets to a jelly in 11 minutes, while in the presence of from 2 to 10% of ordinary turpentine, the gelatinisation takes place only after 12.7 to 26.8 minutes.

Hirschsohn (*Pharm. Zentralh.*, 1903, **44,** 845) recommends the following test for proving the presence of ordinary turpentine or an artificial substitute in Venice turpentine. 1 grm. of the material is treated with 3 grm. of 80% alcohol. If the solution is milky and a portion of the material is precipitated, then at least 10% of artificial or 30% of ordinary turpentine must be present.

## Canada Balsam

**Occurrence.**—This product, also known as balsam of fir, and balsam of Gilead, is the oleo-resinous exudation of the so-called balsam fir, *Abies balsamea*, and allied species.

**Chemical Composition.**—This turpentine contains 18 to 20% of oil, and 2 resins, one soluble in alcohol and the other slightly soluble.

Tschirch[1] and his collaborators have described a large number of acids and resenes obtained from coniferous resins, but the formulæ and even the existence of many of the substances described require confirmation. The table appended gives a résumé of their results.

**Uses and Adulterants.**—Canada balsam is used to a limited extent in medicines, in the preparation of flexible collodion and for mounting microscopic preparations. The usual adulterants of Canada balsam are colophony and common turpentine. Venetian turpentine[2] is sometimes added.

**General Properties.**—Canada balsam is dextrorotatory ($+1°$ to $+4°$), but the essential oil obtained from it is lævorotatory. This balsam has a sp. gr. of about 0.990, and a ref. index of 1.520 at 20°.

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[1] According to A. Tschirch, with the exception of amber, all coniferous oleo-resins are free from esters, consisting solely of resin acids, resenes, and essential oil. These constituents may be separated as indicated on page 220. Only a few of the coniferous resin acids dissolve in ammonium carbonate solution. The majority are amorphous, are dissolved by sodium carbonate (1% solution), and may be separated by crystallisation or precipitation with lead acetate.

The resin acids of copaiba and Zanzibar copal, which are obtained from leguminous plants, present a close resemblance to the coniferous resin acids.

[2] A product known in commerce as "Oregon balsam" and consisting of a mixture of colophony and oil of turpentine much resembling Canada balsam is used as an adulterant of the latter substance (E. Dowzard, *Chem. and Druggist*, 1904, 439). The true so-called Oregon balsam is derived from *Pseudotsuga mucronata*, and its essential oil contains much lævo-pinene. Factitious Oregon balsam of the above composition contains the same proportion of resin as does Canada balsam, and their physical characters are almost identical. The presence of this adulterant is best detected by ascertaining the acid value of the essential-oil-free resin. Colophony has an average acid value of about 165, whilst that of the resin of Canada balsam averages 120 to 124.

This high refractive index differentiates Canada balsam from all other turpentines.  A grain of starch laid in the balsam remains visible, whereas in the case of the other balsams it becomes indistinct or invisible.

Canada Balsam contains if pure 70 to 85% of resin, the remainder being essential oil.  The resin contains about 20% of an indifferent resene, 20% of amorphous canadinic acid, and 60% of a mixture of α- and β-canadolinic acids, with a trace of crystalline canadolic acid.

The Balsam has the following characters:

| | |
|---|---|
| Sp. gr. | 0.983 to 0.997 |
| Optical rotation | +1° to +5° |
| Ref. index | 1.5175 to 1.5220 |
| Acid value | 80 to 90 |
| Ester value | 4 to 8 |

The essential oil has the following characters:

| | |
|---|---|
| B. p. | 160° to 168° |
| Sp. gr. | 0.862 to 0.865 |
| Optical rotation | −26° to −36° |
| Ref. index | 1.4720 to 1.4770 |
| Esters (as bornyl acetate) | Under 1% |

The principal constituent of the essential oil is *l*-pinene.

The acid value of the dry resin varies between 120 and 125.

## Balsam of Copaiba.  Copaiva.  Capivi

**Occurrence.**—Copaiba is an oleo-resin obtained from the trunk of *Copaifera lansdorfii*, and other South American species of *Copaifera*.[1]

The proportions of resin and volatile oil in copaiba are very variable, and hence the viscosity and sp. gr. are far from constant.  The medicinal value of the two constituents of the oleo-resin requires further investigation.

**Adulterants.**[2]—Balsam of copaiba is liable to sophistication in various ways, though gurjun balsam and African Copaiba are the most usual additions.

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[1] See Umney and Bennett, *Pharm. Jour.*, 1901, 1, 324.

[2] A new adulterant of copaiba—segura balsam—a cheaper oleo-resin, has been described by M. Uts (*Pharm. Zentralh.*, 49, 16).  It is a dark brown viscous liquid with a pleasant aromatic odour.  Readily soluble in chloroform, benzene, petroleum spirit and carbon tetrachloride; partially in alcohol.  When steam distilled, it yields from 30 to 40% of essential oil which has a sp. gr. 0.9451 at 15°.

The oleo-resin gives a reddish-brown colour with sulphuric acid; yellowish-green with nitric acid; red-brown with vanillin and hydrochloric acid; a light brown with stannous chloride, in the cold and on heating.  A mixture with Maracaibo balsam causes increase of sp. gr., and the ester value with a lowering of the acid value; the cold saponification value is only slightly affected.  It is probable that but little segura balsam is used as the adulterant, but its essential oil, or a mixture of the oil with segura balsam, is employed.

**Commercial Varieties and General Properties.**—There are several well-defined commercial varieties of copabia balsam which take their names from the port of exportation.

**Maracaibo balsam** is a common commercial copaiba. The essential oil distilled from this balsam is typical copaiba oil having sp. gr. about 0.900 to 0.910, and an optical rotation ranging from $-7°$ to $-35°$. The residue consists almost entirely of resin acid, namely: *β-meta-copaivic acid*, $C_{10}H_{16}O_2$, crystallising in pointed prisms, m. p. 89 to 90°, and *illuric acid*, $C_{20}H_{28}O_3$, melting at 128°.

**Para balsam** is very variable in quality, but is remarkable for its fluidity and its high proportion of essential oil. The resin of this balsam contains, besides indifferent *resenes, para-copavic acid*, $C_{20}H_{32}O_3$, crystallising in pointed and quadratic leaflets, m. p. 145 to 148°, and soluble in ammonium carbonate solution; and *homo-para-copaivic acid*, $C_{18}H_{28}O_3$, m. p. 111°, and insoluble in ammonium carbonate, but soluble in sodium carbonate solution.

**Maturin balsam** is of golden-yellow colour, fairly thick, and is not fluorescent. It has a somewhat more pleasant odour than most varieties of copaiba balsam.

**Maranham balsam** is a thick, golden-brown liquid, and is most esteemed for the manufacture of capsules.

Bahia and Cartagena balsams are also commercial varieties.

**African (Illurin) balsam** is of uncertain botanical origin, though probably derived from a species of *Copaifera*. It is distinguished from other copaibas by yielding a dextrorotatory oil, and its presence in the balsam used in medicine is specially guarded against in the British Pharmacopœia by means of this property. African balsam has a high sp. gr. (0.985 to 1.000), is of fairly thick consistence, exhibits a slight fluorescence, and has a pungent, pepper-like odour, It deposits crystals on standing, and yields about 4% of volatile oil on distillation with steam (see page 310). The acid value of illurin balsam is given as 57 to 60, and the ester value at from 9 to 10. *Illuric acid*, $C_{20}H_{28}O_3$, the chief resin acid of African balsam. forms hexagonal table, m. p. 128° (Tschirch, *Pharm. Central.*, 1891, 337). It is probably identical with the crystalline acid described by Umney and by Peinemann, and possibly also with Fehling's "*oxy-copaibic acid.*" The essential oil of African copaiba has, according to Parry and Bennett, been extensively used for the adulteration of peppermint oil.

**Specific Gravity.**—The specific gravity of copaiba balsam varies considerably and only gives reliable indication of the quality of the article when considered in conjunction with the proportion and characters of the volatile oil present. The thinner varieties of balsam containing a high proportion of oil have a sp. gr. as low as 0.916 (as in the case of Para balsam) whereas the sp. gr. of the thicker varieties often exceeds 0.990, and occasionally reaches 1.000 or even more. The sp. gr. limits are from 0.916 to 0.995, but these figures are sometimes slightly exceeded.

**Optical Rotation.**—As a rule, the colour of copaiba balsam is too deep to allow of the observation of its *optical rotation*, but the optical activity of the essential oil is an important character.

**Essential Oil.**—The proportion of this substance present in copaiba balsam is very variable. In cases where the balsam is intended for distillation the amount of oil is important. The percentage of oil in genuine balsams usually ranges between 40 and 75% rarely much exceeding the latter figure. As a rule, the percentage seldom exceeds 55, except in the case of the low-gravity Para copaiba. As much as 92% of oil has been recorded, but such a sample was probably adulterated with turpentine.

**Oil of Copaiba.**—The estimation of the essential oil present in copaiba is best ascertained from the loss of weight suffered by the sample at about 120°, when, except in rare cases, the residual resin will be hard and friable. The resin should never exceed 60%, and is frequently as low as 35% or even less. For the examination of the characters of the oil, 100 grm. of the balsam should be steam-distilled in the usual way. Generally speaking, the only adulterants which will affect the characters of the oil thus obtained are gurjun balsam, and African balsam of copaiba.[1] The sp. gr. of the oil from genuine copaiba ranges, according to Schimmel & Co., between 0.900 and 0.910, but these limits are too narrow, as pure samples will often yield an oil of sp. gr. 0.898. The limits 0.895 and 0.910 are safer. The optical rotation of oil of copaiba varies between −7° and −35°.

E. J. Parry (*Chem. and Druggist*, 1907, **71**, 518) states that an enormous amount of adulteration is being practised. African copaiba reduces the optical rotation of the essential oil, although the resin still answers the other British Pharmacopœia tests. He

[1] In the presence of African copaiba, the oil obtained by steam distillation will exhibit comparatively feeble lævorotation, or if the proportion be very large, the oil may be dextrorotatory.

believes that at times genuine samples of Maracaibo balsam fall outside the British Pharmacopœia limits, but suggests that in the majority of cases the low rotation is due to some adulterant, probably African copaiba.

In the *Year-book of Pharmacy*, 1908, 59 results obtained by Evans are given relating to samples of Maranham, Maracaibo, and Carthagena copaiba, which shows that the Maracaibo variety consistently gives lower figures than the Maranham variety. Evans thinks that the suggested lower figure of $-7$ may exclude genuine samples. G. Weigel (*Chemist and Druggist*, 1907, **71**, 617) distilled 100 samples of oil and found $[a]_D$ ranging from $-5$ to $-28$. This author believes that if limits were placed from $-5$ to $-25$, 90% of genuine oils would be included.

The oil distilled from pure balsam of copaiba is completely soluble in absolute alcohol and in 4 times its volume of petroleum spirit.

The following figures by J. C. Umney show the properties of the oil from African balsam as compared with those of the oils yielded by Maracaibo and Para balsams:

|  | African | Maracaibo | Para |
|---|---|---|---|
| Per cent. of volatile oil in balsam........... | 32 | 42 | 64.3 to 80.2 |
| Sp. gr. of oil at 15°....................... | 0.9180 | 0.9050 | 0.9060 |
| Rotation in 200 mm. tube.................. | +20.7° | −34.3° | −28.9° |
| Solubility in absolute alcohol at 15°......... | not sol. in 50 | 1 in 1 | 1 in 1 |
| Range of b. p............................. | 260° to 273° | 245° to 255° | 252° to 260° |

No other differences of importance were observed by Umney, except that the oil from the African balsam reduced auric chloride in chloroform solution (with 1% of alcohol), while the other oils did not.

*Copaiba resin* is not now official in the United States Pharmacopœia. According to Umney and Bennett, it is soluble in alcohol, ether, and carbon disulphide, forming acid solutions. 1 grm. should neutralise at least 21.5 c.c. of N/10 alkali when titrated in alcoholic solution with phenolphthalein.

Umney and Bennett (*Pharm. J.*, 1901, **1**, 324) suggest that the official requirements for copaiba balsam should be revised as follows: A more or less viscid liquid, generally transparent and occasionally

fluorescent; yellow or brown, having a peculiar aromatic odour, and a persistent acrid, somewhat bitter taste. Sp. gr., 0.975 to 0.995. Entirely soluble in absolute alcohol, and in 4 volumes of petroleum spirit, the latter solution yielding only a slight filmy deposit on standing. It should evolve no odour of turpentine oil when heated, and should not lose more than 45% when heated in a water-bath for 48 hours. 3 volumes should form a transparent mixture when added to 1 measure of ammonium hydroxide (10%). The volatile oil should have a rotation of −7° to −21° for 100 mm., and should not boil under 250° (absence of African balsam). It should give a negative result with the glacial acetic and sulphuric acids test (p. 316, absence of gurjun balsam). A solution of 1 grm. in 50 c.c. of absolute alcohol should neutralise at least 13.5 c.c. of N/10 alkali hydroxide on titration with phenolphthalein (presence of a sufficient proportion of resin acids).

The same authors have recorded the following characters for 5 specially selected typical samples of copaiba balsam:

| | Bahia | Cartagena | Maracaibo | Maranham | Para |
|---|---|---|---|---|---|
| **Balsam** | | | | | |
| Sp. gr.................... | 0.938 | 0.970 | 0.969 | 0.990 | 0.920 |
| % of oil................. | 49.7 | 41.3 | 42.5 | 41.8 | 62.4 |
| United States Pharmacopœia ammonia test.............. | turbid | clear | clear | clear | turbid |
| Acid value.............. | 33.7 | 56.0 | 50.2 | 81.5 | 33.1 |
| Ester value.............. | 15.3 | 28.0 | 12.1 | 12.8 | 26.9 |
| **Resin** | | | | | |
| Physical characters........... | soft | brittle | firm | brittle | very soft |
| Acid value................. | 73.1 | 135.7 | 80.3 | 136.3 | 68.9 |
| Ester value................. | 73.0 | 45.1 | 49.9 | 36.7 | 87.2 |

The characters of the essential oil from these samples were not distinctive. The sp. gr. ranged from 0.903 to 0.908, and the boiling point from 245° to 275°. The oils were soluble in an equal quantity of absolute alcohol, and their optical rotation for 1 dcm. varied from −7° to −21°. Gildemeister and Hoffmann give the range as from −7° to −35°.

Copaiba resin consisting chiefly of free resin acids, the balsam has a very high acid value, but an insignificant ester value. The following table gives the limits for the analytical results recorded by various observers for the different varieties of balsam of copaiba:

| Variety of balsam | Characters of balsam | | | Essential oil | |
|---|---|---|---|---|---|
| | Sp. gr. | Acid value | Ester value | % | Sp. gr. |
| Angostura............ | 0.980 to 1.009 | 75 to 85 | 7 to 20 | 40 to 45 | 0.906 |
| Bahia................ | 0.980 | 34 to 98 | 5 to 15 | 40 to 45 | 0.908 |
| Carthagena.......... | 0.950 to 0.965 | 56 to 88 | 5 to 28 | 50 to 55 | 0.904 |
| Maracaibo........... | 0.980 to 0.998 | 50 to 98 | 0 to 15 | 50 to 65 | 0.895 to 0.907 |
| Maranham........... | 0.990 | 81.5 | 13 | 42 to 50 | 0.902 |
| Maturin............. | 0.980 to 0.988 | 75 to 85 | 4 to 13 | 45 to 50 | 0.898 |
| Para................ | 0.915 to 0.990 | 25 to 62 | 2 to 33 | 40 to 90 | 0.898 to 0.904 |
| Surinam............. | 0.907 to 0.961 | 15 to 59 | 10 to 18 | 41 to 72 | 0.910 |
| African (illurin)..... | 0.985 to 1.00 | 57 to 60 | 9 to 10 | 40 | 0.918 |
| Gurjun balsam....... | 0.955 to 0.980 | 5.8 to 20 | 1 to 10 | 55 to 82 | 0.915 to 0.930 |

The wide variations recorded above are probably due to certain of the samples being adulterated.

L. F. Kebler (*Amer. J. Pharm.*, 1897, **69**, 577) has published the results of the examination of various samples of commercial copaiba, as have also E. W. Bell (*Pharm. J.*, 1900, **67**, 99) and E. W. Mann (*Pharm. J.*, 1903, **70**, 419). The last-named found that the greater number of the commercial samples examined by him responded to the colour tests for gurjun oil, although in other respects they conform to the description of a genuine sample.

Evans (*Analytical Notes*, 1914, **8**, 28) gives the following figures for 18 pure and 1 adulterated samples of copaiba. In all cases the essential oil was distilled *in vacuo*.

PURE COPAIBAS

| | Balsam values | | | | Essential oil values | | |
|---|---|---|---|---|---|---|---|
| | Acid value | Acid value, non-oily portion | $n_D 15°$ | Ess. oil, per cent | Sp. gr. | $n_D 15°$ | $\alpha_D$ |
| *Para* | | | | | | | |
| 1 | 31.1 | 107.2 | 1.5073 | 71.0 | 0.904 | 1.4994 | −30° 30′ |
| 2 | 30.8 | 102.6 | 1.5085 | 70.0 | 0.903 | 1.4993 | −31° 30′ |
| 3 | 66.5 | 162.0 | 1.5094 | 59.0 | 0.906 | 1.4983 | −17° 40′ |
| 4 | 67.7 | 118.0 | 1.5107 | 42.5 | 0.895 | 1.4943 | −29° 0′ |
| 5 | 42.6 | 152.0 | 1.5076 | 72.0 | 0.903 | 1.4999 | −14° 28′ |
| 6 | 34.0 | 151.0 | 1.5107 | 77.5 | 0.9065 | 1.5026 | −18° 45′ |
| *Maracaibo* | | | | | | | |
| 7 | 91.4 | 170.0 | 1.5172 | 46.0 | 0.902 | 1.4986 | − 8° 20 |
| 8 | 80.0 | 143.0 | 1.5151 | 44.0 | 0.897 | 1.4971 | −10° 0′ |
| 9 | 80.2 | 143.0 | 1.5136 | 44.0 | 0.899 | 1.4975 | − 9° 55′ |
| 10 | 79.1 | 143.0 | 1.5183 | 44.6 | 0.903 | 1.4988 | − 9° 5′ |
| *Maranham* | | | | | | | |
| 11 | 81.3 | 138.0 | 1.5137 | 41.0 | 0.8985 | 1.4968 | −17° 52′ |
| 12 | 86.8 | 150.0 | 1.516 | 42.0 | 0.9045 | 1.4992 | −19° 12′ |
| 13 | 78.2 | 147.5 | 1.5135 | 47.0 | 0.901 | 1.497 | −17° 40′ |
| 14 | 85.4 | 158.1 | 1.5152 | 46.0 | 0.8985 | 1.4966 | −21° 41′ |
| 15 | 84.0 | 168.0 | 1.515 | 50.0 | 0.903 | 1.4978 | −16° |
| 16 | 89.6 | 160.0 | 1.5133 | 44.0 | 0.902 | 1.4977 | −19° |
| 17 | 86.8 | 144.5 | 1.5137 | 40.0 | 0.900 | 1.4967 | −19° |
| 18 | 72.4 | 120.8 | 1.5098 | 44.0 | 0.8965 | 1.494 | −20° 30′ |

## ADULTERATED COPAIBAS

| | Balsam values | | | | Essential oil values | | |
|---|---|---|---|---|---|---|---|
| | Acid value | Acid value, non-oily portion | $n_D 15°$ | Ess. oil, per cent | Sp. gr. | $n_D 15°$ | $α_D$ |
| *Para* | | | | | | | |
| 19 | 77.1 | 167.4 | 1.5100 | 54.0 | 0.8905 | 1.4929 | −29° 12′ |
| 20 | 22.4 | 187.0 | 1.500 | 88.0 | 0.9065 | 1.499 | − 9° 0′ |
| 21 | 31.8 | 156.6 | 1.5057 | 79.7 | 0.9045 | 1.499 | − 7° 0′ |
| 22 | 26.0 | .116.0 | 1.5048 | 77.5 | 0.9025 | 1.5004 | −10° 12′ |
| 23 | 14.5 | 89.2 | 1.5023 | 83.8 | 0.9085 | 1.4991 | −31° 55′ |
| 24 | 77.3 | 143.0 | 1.5117 | 46.0 | 0.892 | 1.4957 | −26° 15′ |
| 25 | 80.4 | 174.0 | 1.511 | 54.0 | 0.8845 | 1.4934 | −34° 15′ |
| *Maracaibo* | | | | | | | |
| 26 | 85.2 | 160.7 | 1.5128 | 47.0 | 0.910 | 1.4975 | − 0° 10′ |
| 27 | 87.5 | 168.3 | 1.5177 | 48.0 | 0.9035 | 1.4981 | − 5° 32′ |
| 28 | 78.0 | 147.0 | 1.512 | 47.0 | 0.903 | 1.4981 | − 7° 45′ |
| 29 | 82.2 | 153.9 | 1.5176 | 46.6 | 0.901 | 1.4987 | −10° 20′ |

Deussen and Eger (*Chem. Zeit.*, 1912, 561) have devised a new method for the examination of oil of copaiba, in order to decide whether the balsam is pure or not. The oil specially considered is that of African copaiba. The method is based on the fact that African copaiba oil contains much more cadinene than does Para copaiba oil. The dihydrochloride of cadinene melts at $117° -118°$, and that of caryophyllene, the principal sesquiterpene of copaiba oil, at $69° - 70°$. By fractionating the oil, as indicated below, and preparing the dihydrochloride from the suitable fractions, a comparison of the melting points of the crude products is possible, and this will give marked indications as to the presence or absence of African copaiba. The dihydrochloride is prepared by dissolving the fraction in ether, and saturating with dry hydrogen chloride gas, washing the separated crystals with ether, and drying on a porous plate. The melting points of the dihydrochlorides obtained from pure and from adulterated oil are shown in the appended table:

| | Fractions at 9 mm. | | | |
| --- | --- | --- | --- | --- |
| | 114°–117° | 117°–122° | 122°–129° | 129°–132° |
| (1) Pure Para Oil— | | | | |
|    Rotation | −8.80° | −11.37° | −12.65° | ........... |
|    Yield | ........... | ........... | 23 % | 15 % |
|    M. p. | ........... | ........... | 75° | 76° |
| (2) +5 % African Oil— | | | | |
|    Rotation | −8.88° | −10.25° | −11.33° | ........... |
|    Yield | ........... | ........... | 25 % | { very small amount |
|    M. p. | ........... | ........... | 85° | 110° |
| (3) +10 % African Oil— | | | | |
|    Rotation | −6.70° | −7.85° | −7.25 | −4° |
|    Yield | ........... | ........... | 18.5 % | 10 % |
|    M. p. | ........... | ........... | 110–112° | 115° |
| (4) +20 % African Oil— | | | | |
|    Rotation | −6.20° | −6.45° | −1.94° | +3.66° |
|    Yield | ........... | ........... | 29 % | 19 % |
|    M. p. | ........... | ........... | 114–115° | 116–117° |

The authors have also shown that caryophyllene yields, when treated with $NO_2$ in ethereal solution, a crystalline nitro-compound, which they have somewhat unhappily termed "nitro-caryophyllene," of the formula $C_{12}H_{19}N_3O_6$; it melts at 159°–160°. The yield of this substance obtained from different oils is variable, and will give some indication of the origin of the oil. They give the following results:

<div align="right">YIELD OBTAINED</div>

From caryophyllene from clove oil................ 50–52%
From Para copaiba oil (1)........................ 9.5–10%
                   (2)........................ 15%
                   (3)........................ 15%
                   (4)........................ 15–16%
From Maracaibo oil (1)........................... 5–6%
              (2)........................... 3%
From Maturin oil................................ 8–9%
From Para oil +10% gurjun oil................. 13.3–14.3%
From Para oil +20% gurjun oil................. 11.7–12.7%
From Para oil +30% gurjun oil................. 10.7–11.7%
From Para oil +50% gurjun oil................. 7.7–8.3%

**Characters of Copaiba Oil.**—The following figures are given by Gildemeister for various types of oil of copaiba (*Die Ätherischen Oele*, 2nd Edition, Vol. II, p. 616).

| Balsam | Sp. gr. | Rotation | Ref. index | Acid value | Ester value |
|---|---|---|---|---|---|
| Para............... | 0.886–0.910 | − 7° to −33° | 1.493–1.502 | 0.1.9 | 0– 4 |
| Maracaibo.......... | 0.900–0.905 | − 2° 30′ to −12° | 1.498 | 0.9–1.0 | 1– 1.6 |
| Bahia.............. | 0.888–0.909 | − 8° to −28° | 1.494–1.497 | 0.5–7.9 | 0–14.9 |
| Maranham.......... | 0.896–0.905 | − 1° 30′ to −22° | ............ | ...... | ...... |
| Cartagena.......... | 0.894–0.910 | − 2° 30′ to −23° | ............ | ...... | ...... |
| Maturin............ | 0.899–0.904 | − 7° 30′ to −10° 10 | 1.497–1.500 | 0–0.6 | 0.9– 3.6 |
| Angostura........... | 0.916 | − 2° 20 | 1.502 | 10.9 | 0 |
| Guiana (British)...... | 0.924 | − 9° | ............ | ...... | ...... |
| Guiana (Dutch)...... | 0.903–0.906 | − 7° 30 to −10° 30′ | ............ | 0 | 6.7 |
| Bolivia............. | 0.916 | +18° | 1.505 | 1.1 | 0.5 |

**Detection of African Copaiba.**—Cocking (*Chemist and Druggist* 1910, **77,** 119) has suggested a method of detecting the so-called African copaiba in genuine copaiba balsam. It consists in distilling the balsam *in vacuo* or with steam and afterwards dividing the resulting oil into 10 equal fractions by distillation *in vacuo*, determining the rotation of these fractions. With pure Maranham and Pará balsam oils all the fractions were lævorotatory and showed a very gradual increase in rotation from the first to the tenth fractions. The differences between the rotations of the tenth and the first fractions ("difference value") were invariably negative and ranged in the case of the separate oil from −3.7 to −7.6°. The rotation of the first fraction was a little below that of the original oil. African copaiba balsam yields an oil of which the separate fractions were dextrorotatory. In this case the rotations show a decidedly higher rate of increase than in the American balsam oil, for which reason the difference value is also much greater, whilst moreover it is positive (about +23°). Gurjun balsam oil gave exclusively lævorotatory fractions. The rotation of the first fraction was higher than that of the original oil, after this it decreased with each fraction, so that here also the difference value is positive (+44.4°). Between the ninth and the tenth fraction there was a sudden decline. In the writer's opinion this method is useless and the deductions drawn quite unwarranted. Further, the slightest deviation from a given method of distillation will give appreciably different results.

**Composition of African Copaiba Oil.**—H. von Soden (*Chem. Zeit.*, 1909, **33,** 428) has examined this oil, the sample in question having a sp. gr. 0.9215, optical rotation +21°, and b. p. from 266° to 270°. The ester value is about 5–6, and the ester value after acetylation about 10. The principal constituent found was cadinene. Schimmel and Co., however (*Report*, April, 1914, 48) have shown that

this sesquiterpene, although very closely related to cadinene, and yielding cadinene hydrochloride, is not, in fact, identical with cadinene. Traces of $\beta$-caryopyllene are also present.

**Detection of Gurjun balsam** : This balsam is the product of several species of Dipterocarpus, and presents a close general resemblance to copaiba. It is said to contain a crystalline substance known as *gurjunol*, $C_{20}H_{28}(OH)_2$, m. p. 126° to 129°, while, according to Tschirch and Weil, a neutral resene, containing $C_{17}H_{28}O_2$, is present. The sp. gr. of gurjun balsam averages about 0.964, while that of the essential oil (which is sometimes present to the extent of 80 to 82%) ranges from 0.915 to 0.930, and hence in its presence the sp. gr. of copaiba oil will be slightly raised. Gurjun oil is usually strongly lævorotatory ($-55°$ to $-130°$), but several specimens of dextrorotatory oil have been met with. As a rule, however, the lævorotation of copaiba oil will be considerably increased by an admixture of gurjun oil. Gurjun oil distils almost completely between 255° and 265°, the main constituent being a sesquiterpene boiling at 255° to 256°, at which temperature a large fraction of the oil passes over.

Copaiba balsam adulterated with gurjun balsam is not quite clear, and frequently exhibits prisms of gurjunic acid under the microscope. According to E. Hirschsohn, gurjun balsam is incompletely soluble in ether, whereas copaiba balsam gives a clear solution. Alcoholic lead acetate solution gives a cloudiness with an alcoholic solution of copaiba, which disappears on warming, whilst with gurjun balsam no reaction takes place.

L. B. Kebler (*Amer. J. Pharm.*, 1895, **67**, 394) considers that no dependence can be placed on the physical characters of the sample. He considers that the ammonia test is misleading, the acid value unreliable, and Hager's colour test unsatisfactory, especially if the proportion of gurjun balsam be less than 25%. The most reliable colour test for the identification of gurjun balsam is the "Turner reaction" (*Amer. J. Pharm.*, 1908, **80**, 14): 3 to 4 drops of balsam are dissolved in 3 c.c. of glacial acetic acid and the mixture is carefully poured on to the surface of 2 c.c. of concentrated sulphuric acid contained in a small test-tube. When pure copaiba balsam is present, the acetic acid solution remains colourless or assumes a pale yellow tint, whereas in the presence of Gurjun balsam a dark violet coloration of the acetic acid solution is produced. The test is best applied to the essential oil distilled from the sample. Turner states that

5% of Gurjun balsam can be detected by this means, but Utz (*Chem. Rev. Fett Harz-Ind.*, 1908, **15**, 220), by collecting and testing the oil fraction b. p. above 200°, was able to identify 2%. The colour test may always be applied with advantage to the distilled oils, since certain fish oils give evanescent colours, and these oils are not of course found in the distillate. Oil of valerian is also said to give a similar coloration.

**Oil of turpentine** may be readily detected in copaiba balsam by steam-distilling the sample, the volatile oil of the balsam and the oil of turpentine passing over. The latter distils before the copaiba oil, oil of turpentine, boiling at about 160°, and oil of copaiba at 240° to 250°. The odour of the turpentine can be detected when the first few drops of distillate are heated on a watch-glass, by which means 2% or 3% of the adulterant may be detected. An idea of the amount of oil of turpentine present may be obtained by observing the sp. gr. and b. p. of the distilled oil. The presence of oil of turpentine in copaiba balsam reduces the sp. gr. and lowers the acid and ester values, while it increases the % of essential oil, which has a lower sp. gr. and opt. rot. than genuine oil of copaiba.

**Fatty Oils.**—The presence of fatty oils in copaiba balsam renders the separated resin soft, and reduces the % of essential oil in the sample. The sp. gr. and acid value of the sample are also lowered, while the ester value is raised.

According to Utz (Schimmel & Co. Report, April, 1906, 13) commercial samples of copaiba balsam in Abbe's refractometer show a ref. index varying from 1.5088 to 1.5288. Gurjun balsam gives similar values, but the presence of fatty oils or turpentine lowers these figures considerably.

For the detection of *castor oil* in copaiba balsam L. Maupy (*Jour. Pharm. Chim.*, 1894, 362) recommends the following method, based on the fact that castor oil yields *sebacic acid* and *caprylic alcohol* on dry distillation with excess of potassium hydroxide: 10 grm. of the sample are heated with dry potassium hydroxide in a silver dish. The mass is stirred and heated until all the volatile oily matters are driven off. In the presence of castor oil, the odour of caprylic alcohol will be noticeable. On cooling and thoroughly separating the upper resinous layer, the lower white liquid portion is treated with 50 c.c. of water, boiled and filtered. Sebacic acid separates out on

cooling if the sample contained castor oil. The acid may be further identified by converting it into the lead salt.

For the estimation of *fatty oils*, J. Muter (*Analyst*, 1876, **1**, 160) recommended a process based on the insolubility of oleate and ricinoleate of sodium in ether-alcohol, and the solubility of the sodium salts or copaiba resin acids in the same solvent.

**Colophony.**—L. E. Walbaum (*Pharm. Zentrh.*, 1907, **48**, 437), has given the following method for the detection of colophony in copaiba balsam: 4 c.c. of a 1% solution of ammonia and 1 c.c. of acetone are mixed; to this solution 2 grm. of the balsam dissolved in 6 grm. of ether are added. The whole is well shaken, then allowed to stand until the lower aqueous layer is clear. In the presence of colophony this layer will be darker in colour than a solution containing a grm. of balsam in 5 c.c. of absolute alcohol prepared for the purpose of comparison. This colour reaction is only produced by colophony; Canada balsam, mastic, dammar, sandarac, etc., mixed with copaiba balsam give no such colour under similar conditions. This test will readily detect 2% of colophony and even 0.5% will give a definite indication.

*Cativo*, from *Prioria copaifera*, presents no similarity to copaiba balsam, although it has been supposed to resemble it. (See E. M. Holmes; J. C. Umney; *Pharm. J.*, 1902, **69**, 296.)

### OLEORESIN OF CUBEBS

The oleoresin of the fruits of *Piper cubeba*, is extracted with ether. It is a green viscous liquid and contains the following as its chief constituents:—

1. An essential oil, whose characters are

| | |
|---|---|
| Sp. gr. | 0.912 to 0.932 |
| Opt. rot. | $-25°$ to $-42°$ |
| Ref. index. | 1.4930 to 1.4970 |

It contains terpenes, sesquiterpenes, cubeb-camphor and a crystalline sesquiterpene alcohol $C_{15}H_{25}.OH$.

(2) Fatty oil.

(3) Cubebin, a substance crystallising in white odourless needles, melting at about 128°. The constitution is not yet settled.

(4) Resins. There are several resins present, some of an acid nature, some neutral.

Oleoresin of cubebs has a specific gravity from 0.985 to 1.020 at 15°, rarely rising to 1.050 where the essential oil is low. The refractive index varies between 1.500 and 1.5100.

Between 20 and 40% is lost on prolonged heating to 110°, being the essential oil present. The acid value lies between 15 and 30, and the saponification value between about 50 and 65.

The examination of the residues after driving off the essential oil has not been systematically carried out. This would be of considerable value from an analytical point of view, as the varying amounts of essential oil present make comparisons difficult.

## Capsicin

The oleoresin of the Capsicum fruit is usually known as Capsicin. It is prepared by means of various solvents, of which ether, alcohol and acetone are the most commonly used. Its composition cannot, therefore, be constant, on this account. It contains a fatty oil, an essential oil, resins, a crystalline substance, capsaicin, and possibly an alkaloid known as capsicin. Capsaicin is the pungent principle of capsicum fruit or cayenne pepper. It is a colourless, crystalline substance of the formula $C_9H_{17}.CO.NH.CH_2(C_6H_3)(OH)(OCH_3)$. It is the vanillylamide of a decenoic acid. It melts at about 63°–65°. It is present to the extent of under 0.1%, so that is obviously intensely pungent.

The characters of the resinous matter await investigation. Capsicin is a brownish red viscous mass of intensely pungent taste. Indeed, it should be tasted with great caution or considerable pain may result.

When prepared with ether as the solvent, Capsicin is soluble in acetone, ether, chloroform and petroleum spirit, but not to a great extent in 90% alcohol. When prepared with alcohol, the oleoresin contains less fatty oil, and is, of course, easily soluble in alcohol.

The specific gravity varies between 0.925 and 0.940, occasionally down to 0.915. The refractive index is from 1.4650 to 1.4790 at 20°.

When heated on the water bath capsicin should not lose more than 1 to 2% in weight. Any greater loss indicates an excess of solvent left in the oleoresin. Traces only of ash should be allowed. The acid value varies from 90 to 100 when alcohol has been used as the solvent, and from 100 to 108 when other solvents have been used. Thes values however require confirmation and must be accepted

with reserve. The saponification value should lie between 190 and 210.

## Gingerine

The oleo-resin of the ginger rhizome is commonly known as gingerine. The powdered rhizomes are usually exhausted with ether, but alcohol, petroleum spirit and acetone are also used as solvents. The dark red-brown oleo-resin contains the essential oil of ginger together with resins, wax, fatty matter and a pungent constituent known as gingerol.

Essential oil of ginger is an oil having a pleasant aroma of the rhizome, but not much pungency. It is a liquid of specific gravity 0.875 to 0.890 at 15.5° and is lævorotatory −25 to −55°. The principal constitutent is a sesquiterpene, zingiberene. Gingerol or zingiberol is probablly a mixture of phenolic substances which are responsible for the pungency of the rhizome. Its composition is not yet accurately determined.

The resins present are also substances of an indefinite nature. The oleo-resin, when prepared with ether or acetone, has a specific gracity 1.026 to 1.045 at 15.5°; when prepared with alcohol this figure is highly raised, and when prepared with petroleum spirit, it is rather below 1.000.

The refractive index varies between 1.5150 and 1.5250 at 20°. A normal oleo-resin will lose between 10 and 20% of its weight when heated to constant weight on a water bath. The acid value varies between 10 and 16 and the saponification value between 100 and 120. The only probable adulterant is the oleo-resin of capsicin. Garnett and Grier elaborated a method by which this adulterant can be detected. One grm. is digested for 15 minutes on a water bath with an alcoholic solution of caustic alkali. The alcohol is evaporated and the residue is acidulated with hydrochloric acid. The liquid is then extracted with ether. If the residue on evaporation of the ether is hot and pungent to the taste, capsicum is indicated. Gingerol is estimated by boiling about 1 grm. with several successive portions of petroleum spirit and the petroleum spirit is evaporated. The residue is dissolved in 60% alcohol, and the alcoholic solution is shaken with petroleum spirit. The alcohol is then removed by evaporation and the residue extracted three times with ether the ether evaporated and the residual gingerol weighed.

The average amount is from 22 to 30%, or when manufactured by petroleum spirit extraction up to 40%.

## Oleo-resin of Male Fern

### (Extract of Male Fern)

This substance is the ethereal extract of the dried rhizome of *Dryopteris Filix-mas*, the male shield fern. ·

It is employed to a considerable extent in medicine as an anthelmintic, and, as it is comparatively expensive, it is frequently adulterated, principally with castor oil.

The oleo-resin contains the following constituents.

1. An essential oil in small amount. This is a clear yellow liquid of specific gravity 0.85 to 0.86 at 15.5°, and consists mainly of the fatty acid esters of hexyl and octyl alcohols, the fatty acids ranging from propionic to caproic acids.

2. Fatty oil consisting of the glyceryl esters of oleic, palmitic, cerotic and butyric acids. This is present to the extent of about 70%.

3. Filicic acid, $C_{35}H_{38}O_{12}$, crystallising in small yellow plates melting at 184°–185°. This is present to the extent of 6 to 14%.

4. Albaspidin. This is a colourless crystalline substance, melting at 147°–148°, of the formula $C_{25}H_{32}O_8$, and is probably one of the active ingredients of the drug.

5. Flavaspidic acid, $C_{24}H_{28}O_8$, exists in two isomeric forms, of which the $\alpha$-variety melts at 92° and the $\beta$-variety at 156°.

6. Aspidinol, $C_{12}H_{16}O_4$, melts at 156°–161°.

7. Flavaspidin is closely related to flavaspidic acid, and melts at 199°.

8. Filmarone, $C_{47}H_{52}O_{16}$, is a yellow amophorus powder melting at about 60°, and is present to the extent of 5%.

The therapeutic value of male fern is due to a number of its constituents, of which filmarone is the most important. The analysis of the extract would include the following estimations.

*Colour.* When prepared from fresh rhizomes it is of an olive green colour when spread in a very thin layer on a porcelain tile. A brown to brownish-green colour denotes the use of old and inferior rhizomes, whereas a very brilliant pea is indicative of added chlorophyll.

*Specific Gravity.* E. J. Parry, (*Chemist and Druggist*, **79,** 749; **83,** 231), shows that commercial samples with specific gravities of about 0.980 were universally adulterated, and stated that the genuine extract should have a specific gravity of not less than 1.000 at 15.5°. This is now universally accepted.

*Refractive Index.* E. J. Parry (*loc. cit*) gives the refractive index at 20° as not less than 1.5000. This figure is confirmed by other observers, and it may be taken that the higher the refractive index, the richer the extract is in filicin. Harrison and Sef have examined a number of samples and give 1.4995 to 1.5157 at 20° as the refractive indices observed.

*Loss in Weight on Heating.* If the extract be heated on a water bath, not more than about 5% should be lost. Any loss substantially above this is due to unevaporated solvent.

*Acid Value.* This figure should, with normal samples, be between 55 and 80.

*Saponification Value.* E. J. Parry (*loc. cit*) showed that the saponification value would not be lower than 230 for normal extracts containing about 22% of crude filicin. The values 225 to 260 may be taken as fair limits.

*Crude Filicin.* The estimation of the crude filicin, which is a mixture of active constituents, is best carried out by the method of Fromme, which is official in most pharmacopœias.

Not less than 20% (usually 22–28%) should be obtained. 5 grm. are dissolved in 30 c.c. of ether, and 100 c.c. of a 3% solution of barium hydroxide are added. The mixture is well shaken, and the aqueous layer is run off. This is acidified with dilute hydrochloric acid and extracted with ether three times. The ethereal solution is evaporated and the crude filicin weighed.

Hausmann (*Arch. Pharm.*, **237,** 544) gives the following test for the oleo-resin of *Dryopteris spinulosa,* which is sometimes used in admixture with the official rhizomes. The test is based on the fact that the oleo-resin of *D. spinulosa* contains aspidin. A small amount of the crude filicin obtained as above, is dissolved in a very small amount of absolute ether, and the solution placed in a dessicator. If aspidin is present, the thick solution will deposit needle-like crystals in a few hours, which can be easily observed under the microscope. Otherwise, nothing but granular matter will be deposited.

## Oleoresin of Parsley

This oleoresin is usually sold under the name Apiol, which is, in reality the name of its active constituent.

It is the ethereal extract of the fruit of *Petroselinum Sativium* (*Carum Petroselinum*).

It is a green viscous liquid containing a considerable proportion of essential oil of parsley, fatty oil and resins.

The essential oil has the following characters:—

| | |
|---|---|
| Sp. gr. | 1.040 to 1.101 |
| Opt. rot. | $-4°$ to $-10°$ |
| Ref. index at 20° | 1.512 to 1.525 |
| Ester value | 1 to 8 |

The composition of the oil varies considerably with the locality in which the fruit is grown. German oil contains apiol as its chief constituent with only traces of myristicin. French oil, however, contains much myristicin and little apiol.

Apiol is an allyl-dimethoxy methylene-dihydroxybenzene, of the formula $C_{12}H_{14}O_4$. It melts at 30° and boils at 294°. The resins have not been carefully investigated.

The characters of commercial "apiol" are very variable, because some samples are manufactured with ether and others with alcohol. According to Du Mez, when prepared with ether its specific gravity is about 0.940 at 15.5°, but this figure must be taken with reserve. Good commercial samples usually have a specific gravity of 1.075 to 1.100 or thereabouts. The refractive index is around about 1.480 to 1.490 at 20°. The acid value is about 8 to 50 according to the age and method of preparation. The saponification value is usually between 130 and 175.

Yellow apiol, free from wax and fat, has a specific gravity about 1.125 at 15.5°.

## Storax

Storax or styrax is a pathogenic secretion of the injured bark of *Liquidambar orientalis*, a native of the South-west of Asiatic Turkey. The crude storax of commerce contains from 20 to 30% of organic débris, the purified balsam being prepared by solution in alcohol, filtration and evaporation of the solvent. Storax is used both in

medicine and in perfumery, and is a viscous mass of sweet and penetrating odour.

Its constituents are: a resinous material consisting of a free alcohol, storesinol, together with its cinnamic ester; ethyl cinnamate, phenyl-propyl cinnamate, cinnamyl cinnamate (styracin), vanillin and free cinnamic acid. The purified balsam should have the following characters:—

```
Acid value........................... 55 to 95
Ester value.......................... 90 to 150
Sp. gr............................... 1.105 to 1.115 at 100°.
Total cinnamic acid.................. not less than 20%
```

The storax of the British Pharmacopœia (1914) is purified by solution in alcohol, filtration, and evaporation of the solvent.

It should not lose more than 5% when heated on a water bath for an hour. Its acid value is 60 to 90, and ester value 100 to 146. It should yield at least 20% of cinnamic acid when tested as follows: 2.5 grm. are dissolved in 25 c.c. of $N/2$ potassium hydroxide, and boiled for an hour under a reflux condenser. It is neutralised with $N/2$ sulphuric acid, the alcohol evaporated and the residue dissolved in 50 c.c. of water. The solution is washed with 20 c.c. of ether, the ether washed with water, and the water added to the original aqueous solution. The solution is acidified with dilute sulphuric acid and extracted 4 times with 20 c.c. of ether. The ethereal extract is washed with water, transferred to a flask and the ether evaporated. To the residue 100 c.c. of water are added, and the liquid boiled for 15 minutes under a reflux condenser. The solution is filtered hot, cooled to 15.5° and the cinnamic acid separating is collected on a tared filter paper. The residue is extracted by the filtrate, until no more crystals separate. The filter paper is dried in a dessicator and weighed. 0.03 grm, should be added to the weight of cinnamic acid found, to correct for the solubility of the acid in water.

A good deal of the storax of commerce has been deprived of much of its odourous constituents. This question has been investigated by J. C. Umney (*P. & E. O. R.* 1911, 126). He gives the following figures for a number of low grade and adulterated samples.

| Acid value | Ester value | Cinnamic acid, % |
|:---:|:---:|:---:|
| 68.9 | 111.9 | 19.0 |
| 67.1 | 120.9 | 15.2 |
| 96.4 | 94.0 | 14.1 |
| 95.9 | 64.5 | 11.6 |
| 111.6 | 63.8 | 11.7 |
| 101.5 | 92.4 | 9.3 |
| 93.7 | 84.4 | 8.2 |
| 97.1 | 90.2 | 8.3 |
| 99.4 | 30.3 | 7.6 |
| 110.3 | 82.8 | 7.5 |
| 107.0 | 81.1 | 5.6 |
| 99.7 | 14.5 | 4.0 |
| 100.1 | 79.6 | 3.5 |
| 96.5 | 72.4 | 2.5 |

### Balsam of Tolu

Balsam of Tolu is the product of the trunk of the tree *Myroxylon Toluifera*, a tree indigenous to New Granada. It is an aromatic balsam exuding from incisions made in the bark. When fresh it is a soft, tenacious mass, becoming harder on keeping and eventually quite brittle in cold weather. Its odour is fragrant and aromatic.

Its constituents are free cinnamic acid (12 to 15%); free benzoic acid (about 8%); benzyl benzoate; benzyl cinnamate; and resin (about 70%) consisting of the cinnamic and benzoic esters of a complex alcohol known as toluresino-tannol. Traces of vanillin are present. The total free and combined benzoic and cinnamic acids amount to about 35%.

Ordinary colophony is sometimes used as an adulterant, but the usual sophistication is the natural balsam from which the aromatic substances have been abstracted.

Genuine balsam of Tolu would have the following characters:

```
Acid value.................................   100 to 150
Ester value................................    30 to 60
Saponification value.......................   150 to 205
Sp. gr.....................................   1.090 to 1.110
Ref. index at 60°..........................   1.5850 to 1.6020
```

It yields 20 to 30% of cinnamic acid, estimated by the method described under styrax.

The requirements of the British Pharmacopœia (1914) for Balsam of Tolu are as follows:

"It is soluble in 90% alcohol, the solution being acid to litmus. Acid value 107.4 to 147.2 Saponification value 170 to 202. If 5 grm. are gently warmed with three successive portions of 25, 15, and 10 c.c. of carbon disulphide, the solution yields, when evaporated to dryness, a distinctly crystalline residue, which, when tested as described under 'Styrax Præparatus' (*q. v.*) yields not less than 1.25 grm. of balsamic acids." Pure balsam of Tolu should yield about 25% to carbon bisulphide. A lower amount indicates adulteration with exhausted balsam.

Colophony may be detected by the Storch-Morawsky reaction, or by shaking the petroleum spirit extract with a 0.1% solution of copper acetate, when, in the presence of colophony, the petroleum spirit will be coloured brilliant green.

A method is described for estimating cinnamic acid and cinnamein in vol. 3.

## Benzoin

This important aromatic balsam will be found described in volume 3, under "aromatic acids," so that its description in the present volume will be confined within narrow limits.

Siam benzoin is the most esteemed variety of benzoin and is, for the most part, collected in the Siamese province of Luang Prabang, from a tree which has not been definitely identified, but which may be *Styrax Tonkinense*.

Siam benzoin contains as its principal constituent the benzoic ester of the alcohol lubanol. This substance, $C_{17}H_{16}O_4$, is a crystalline substance melting at $72°-73°$. There are also present benzoates of other alcohols, including siaresinol, and an acid termed siaresinolic acid. Traces of vanillin are also present. The total amount of benzoiic acid present is from 30 to 38%. Up to 3–4% of cinnamic acid n the form of esters is also present. A normal Siam benzoin free from dirt and sweepings should contain at least 90% of matter soluble in alcohol, and not more than 3% of mineral matter. Sumatra benzoin is undoubtedly the product of *Styrax benzoin*. It contains lubanol in the form of esters, principally the cinnamate, with some benzoate, and an alcohol which is probably identical with Siaresinol. Benzaldehyde, vanillin, phenyl-propyl cinnamate and

styrol are also present. The amount of combined cinnamic acid is about 10%, and the free cinnamic acid about 7%. Sumatra benzoin should contain from 75–85% of matter soluble in alcohol, and should not yield more than 5% of ash. The following are average figures for the principal varieties of benzoin

### SIAM BENZOIN

Mineral matter (ash)............................ 0.5 to 3%
Soluble in 90% alcohol........................... 88 to 96%
Acid value...................................... 130–170
Ester value..................................... 45–75

### SUMATRA BENZOIN

Mineral matter (ash)............................ 0.5 to 5%
Soluble in 90% alcohol........................... 75–85%
Acid value...................................... 100–145
Ester value..................................... 50–120

The Benzoin of the British Pharmacopœia is Sumatra benzoin, and must contain not less than 85% of matter soluble in 90% alcohol, and not more than 5% of ash.

For the estimation of aromatic acids etc. volume 3 should be consulted.

### Balsam of Peru

Balsam of Peru is an oleo-resinous liquid obtained from the trunk of *Myroxylon pereiræ*, a tree found freely in the forests of San Salvador. The secretion is pathological and not normal, being induced by beating and subsequently scorching the bark.

It is a viscid, reddish brown liquid of highly aromatic odour, and is used in medicine and in perfumery. This is the only commercial variety, the pale coloured balsam obtained from the fruit being rarely seen in commerce.

Being somewhat expensive, Balsam of Peru is often adulterated. Fatty oils, colophony and gurjun balsam are met with from time to time as adulterants, but so-called artificial Balsam of Peru is, to-day, the principal adulterant.

The specific gravity of a genuine Balsam should fall between 1.135 and 1.162 at 15.5°. The refractive index varies between 1.5880 and 1.5960 at 25°, a figure which is lowered by the addition of so-called synthetic balsam.

The mixture of esters of cinnamic acid and benzoic acid is known as cinnamein, and this is present to the extent of 50 to 66%. The requirements of the British Pharmacopœia (1914) for Balsam of Peru are as follows:

One volume is soluble in 1 volume of 90% alcohol, but the solution becomes turbid on the further addition of 2 or more volumes of the alcohol. Specific gravity 1.140 to 1.158 at 15.5°. It is free from alcohol. It yields at least 57% of cinnamein having a saponification value of at least 235 when tested as follows: 1 gr. of the balsam is dissolved in 30 c.c. of ether, and extracted with 20 c.c., and again with 10 c.c. of semi-normal sodium hydroxide. The alkaline solution is washed with 10 c.c. of ether, which is added to the original ethereal solution. The ethereal solution is twice washed with 5 c.c. of water, and the ether evaporated cautiously in a tared wide mouth flask. 1 c.c. of absolute alcohol is added, the substance dried for 30 minutes at 100°, and weighed. The cinnamein thus obtained should weigh at least 0.57 gr., and should have a saponification value of not less than 235.

Treuss has examined five samples of authentic origin and gives the following figures:

|  | SP. GRAVITY | CINNAMEIN, % | ESTER VALUE OF CINNAMEIN |
|---|---|---|---|
| 1. | . . . . . . | 61 | 240 |
| 2. | 1.1404 | 64.7 | 260 |
| 3. | 1.1408 | 66 | 260 |
| 4. | 1.1612 | 50.8 | 249.8 |
| 5. | . . . . . . | 37.7 | . . . . . |

Sample No. 5 was not a normal sample, but was made by extracting the bark with ether.

Dieterich gives the following values for three samples:

|  | 1 | 2 | 3 |
|---|---|---|---|
| Acid value.................. | 77.46 | 76.92 | 27.34 |
| Ester value................. | 165.61 | 137.42 | 137.67 |
| Saponification value........... | 243.07 | 214.34 | 215.01 |
| Cinnamein, etc.............. | 71.41% | 77.56% | 76.63% |
| Resin esters................ | 15.7% | 13.18% | 17.62% |
| Insoluble in ether............ | 4.38% | 4.31% | 3.57% |

His figures must be regarded with suspicion, as the method of estimation of the cinnamein is, apparently, not that usually employed.

High acid values indicate the presence of colophony, which is also indicated by extracting the Balsam with petroleum spirit

and then shaking the petroleum spirit with a dilute solution of copper acetate. In the presence of colophony, the petroleum spirit becomes bright green in colour.

Artificial balsam of Peru is usually based on benzyl benzoate. Natural balsam of Peru has an iodine value of 40 to 45, whilst most artificial cinnamein has a much lower iodine value. This, however, can be adjusted by the use of a little colophony.

The following tests have been recommended for the detection of artificial Balsam of Peru. Two grm. are shaken with 10 c.c. of petroleum spirit, the petroleum spirit evaporated, and the dry residue treated with 2.5 c.c. of nitric acid (sp. gr. 1.38); the genuine balsam will give a golden yellow, and not a brown, colour. Or, if an ethereal solution of the sample be carefully poured on to the surface of strong sulphuric acid, and a little hydrochloric acid be carefully added, a ring appears at the junction of the liquids, which is red below and green above, in the presence of artificial balsams.

### Nauli Gum

Nauli gum is a recently investigated oleo-resin obtained from the Solomon Islands. It was examined by the chemists of the Imperial Institute (*Bulletin*, XIX, 4).

It occurs in fairly soft lumps with a marked odour of aniseed. Its composition was as follows:—

| | |
|---|---:|
| Moisture | 2.5% |
| Essential oil | 10.4 |
| Resin | 81.8 |
| Matter soluble in water and alcohol etc. | 5.3 |

The essential oil had the following characters:—

| | |
|---|---:|
| Sp. gr. at 15.5° | 0.959 |
| Opt. rot. | −25.9° |
| Ref. index | 1.5348 |
| Acid value | 0.65 |
| Ester value | 1.6 |
| Ester value after acetylation | 24.6 |

It contains a considerable amount of anethol. The resin, purified by solution in alcohol, melts at 69–71°, and has an acid value of 9 and an ester value about 16.

### Ladanum Resin

Ladanum, or labdanum, resin, is a secretion from the leaves of several species of *Cistus*, especially *C. creticus* and *C. ladaniferus*,

and to some extent *C. cypricus*. For the exact botanical relationships of the plants yielding the oleo-resin a paper by E. M. Holmes (*P. & E. O. R.* 1911, 155) should be consulted.

A good deal of pure ladanum resin, which is very highly valued for perfumery purpose, is produced in Spain, where no less than 16 species of *Cistus* have been recognised. The Cretan product is very frequently adulterated.

The resinous matter is, to a considerable extent, collected from the beards of goats and the fleece of sheep who brouse upon the foliage, and the resinous matter is then scraped from the animals. It is also collected by scraping, or boiling the branches in water. Ladanum occurs in dark brown to black viscid masses, of intense "oriental" heavy odour. It has been difficult to obtain authentic samples, so that the following analytical values must be accepted with reserve.

Dieterich gives the following figures:—

|  | ACID VALUE | ESTER VALUE |
|---|---|---|
| French commercial | 90.37– 98.4 | 102.1–120.3 |
| German commercial | 51.9 – 54.7 | 162 –168.4 |
| Cretan commercial | 113.8 –114.8 | 87.9–88 |

According to E. J. Emmanuel the oleo-resin contains:

| Ether soluble resin | 48 |
|---|---|
| Alcohol soluble resin (after ether) | 17 |
| Essential Oil | 2 |
| Ladaniol | 0.8% |
| Gummy matter | 3.5 |

Ladaniol is a white crystalline substance melting at 89°, and is probably identical with champsacol extracted from champaca wood oil.

The crude resin varies considerably in composition according to the amount of earthy matter with which it is associated. Some specimens contain only 20% of resinous matter and 70% of earthy impurities. But when the ash value is not more than 5 to 6%, the resinous matter (with oil) will vary from 65 to 85%.

The essential oil from ladanum resin usually has the following characters:

| Specific gravity at | 0.922 to 1.071 |
|---|---|
| Optical rotation | ±0° |
| Refractive index at 20° | 1.4493 |

It contains acetophenone and another ketone, which has the formula $C_9H_{16}O$. This ketone has the constitution.

$$\begin{array}{c}
CH.CH_3 \\
H_2C \quad\quad CO \\
H_2C \quad\quad C(CH_3)_2 \\
CH_2
\end{array}$$
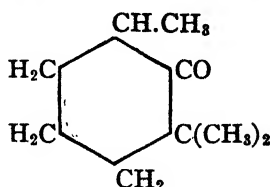
Roure Bertrand Fils, however (*Bulletin*, 1920 *October*, 27) have distilled the pure oleo-resin from *Cistus ladaniferus*, and obtained an oil having the following characters:—

Sp. gr. at 1.55°................................ 0.903
Opt. rot...................................... −12°
Ref. index.................................... 1.4800 at 12.5°
Acid value.................................... 3.7
Ester value................................... 18.67

The distillation waters, when extracted by petroleum spirit gave a small amount of essential oil of finer odour, which had a specific gravity 0.9755 at 15.5°, optical rotation −2°40′, and ester value 22.4.

## GUM-RESINS

The gum-resins constitute a group of natural products which occur as exudations from various plants. These products consist of a mixture of gums with various resins, a small percentage of essential oil, and traces of colouring and undefined matters.

The gum-resins occur in commerce either in tears or masses. The tears are the purer form, as they usually consist of the pure exudation, whereas the latter variety is liable to accidental admixtures, such as woody fibre, etc., besides intentional adulterations of a varied kind. Stones, sand, gypsum, etc., are among the mineral sophistications met with, and adulteration with colophony and other low-priced resinous matters is also practised.

When the natural gum-resins are treated with water, gum, sugar and other carbohydrates are dissolved, but the extraction is apt to be imperfect owing to the protective action exerted by the resionus constituents. A better method of proximate analysis is to treat the substance with alcohol of 95% strength, which dissolves the resinous matters, leaving the carbohydrates practically intact, and

these can be readily extracted with water, any woody fibre or added mineral matters being left as a residue.

## AMMONIACUM

This gum-resin is the product of *Dorema ammoniacum*, one of the *Umbelliferæ*.[1] It occurs in commerce in tears, and in masses of agglutinated tears, which are apt to contain extraneous matters. At ordinary temperatures ammoniacum is hard and brittle, but softens by the heat of the hand. It has a faint, somewhat unpleasant odour, which is accentuated on warming.

A specimen of ammoniacum examined by Tschirch, Luz, and Osterle contained 3.5% of matter insoluble in alcohol and water, in addition to the salicylic ester of *ammoresinotannol*, $C_{18}H_{29}O_2.OH$; traces of free salicylic acid; volatile acids, such as acetic and caproic acids; and about 0.5% of essential oil. No sulphur or umbelliferone could be detected.

The following analyses of apparently authentic samples of ammoniacum have been recorded:

| Number | Ethereal oil, % | Water, % | Ash, % | Gum, % | Resin, % | Observer |
|---|---|---|---|---|---|---|
| 1 | 1.27 | 5.10 | 2.00 | 26.10 | 65.53 | Plugge |
| 2 | .............. | .............. | .............. | 22.4 | 72.0 | Buchholz |
| 3 | .............. | .............. | .............. | 18.4 | 68.6 | Bracounot |
| 4 | .............. | .............. | .............. | 19.3 | .............. | Moss |
| 5 | 1.43 to 6.68 | 0.81 to 3.27 | 2.02 to 3.27 | ...... | 47.2 to 69.2 | Hirschsohn |

According to some authorities, a small quantity of gelatinous matter and sugar are also present.

By dissolving ammoniacum in a 60% aqueous solution of chloral hydrate and pouring the solution into strong alcohol, Mauch obtained 21% of pure gum.

**Identification and Analytical Data.**—5 grm. of finely powdered material are boiled for 15 minutes with about 13 c.c. of fuming hydrochloric acid and filtered. The resulting clear filtrate, on being carefully supersaturated by adding ammonia water, should display no blue fluorescence with reflected light.

The turbid liquid, obtained by boiling 1 part of ammoniacum with 10 parts of water produces a dirty reddish-violet colour with ferric chloride solution (Tschirch). The ignited ammoniacum should not

[1] The so-called African ammoniacum is obtained from *Ferula tingitana*, and differs from the ordinary or Persian product in containing *umbelliferone* (compare Galbanum, page 97).

leave more than 5% of ash. Dieterich states 10%. These tests easily differentiate this resin from galbanum.

The following analytical limits and characters of varieties of ammoniacum have been recorded:

| | A. Kremel | | E. Dieterich | | Beckurts and Brüche | |
| --- | --- | --- | --- | --- | --- | --- |
| | Persian | African | Crude Persian | Purified Persian | Purified Persian | Persian in tears |
| Sp. gr............... | ........ | ....... | ........ | ........ | 1.19 to 1.21 | 1.20 |
| Ash, %............. | ........ | ....... | ........ | ........ | 0.79 to 4.47 | 3.84 |
| Resin soluble in 96% alcohol........... | ........ | ....... | 46 to 88 | 66 to 76 | 59 to 68 | 56 |
| Acid value (of resin) | 100 to 112 | 59 | 57 to 105 | 79 to 135 | 69 to 80 | 70 |
| Ester value (of resin) | 30.6 to 50.5 | 123 | 64 to 91 | 73 to 98 | 19 to 38 | 35 |

Squire has given the following values:

Ash.................................... 2.15%–7.05%
Acid value.............................. 101–106.7
Ester value............................. 162.9 –176.9
Gum................................... 9.8 %– 23.9%

According to Gregor and Bamberger, the methoxyl value of ammoniacum ranges from 8.6 to 11.0.

The only adulterant usually met with in specimens of ammoniacum is the so-called African gum ammoniacum, the product of *Ferula tingitana*. This may be detected in the following manner. If about 60 grm. be powdered and boiled for fifteen minutes with about 15 c.c. of strong hydrochloric acid, the liquid cooled and filtered, and then rendered alkaline with solution of ammonia, the liquid should not be fluorescent. In the presence of either African ammoniacum or gum gallanum a blue fluorescence will be seen in the liquid. Ammoniacum of good quality should contain at least 60% of resin soluble in alcohol, and should not leave more than 7% of ash.

The essential oil from ammoniacum has the following characters:

Sp. gr. at 15.5°.............................. 0.885  to 0.894
Opt. rot................................... +1° to +3°
Ref. index at 20°.......................... 1.4723 to 1.4808
Acid value ................................ 1 to 4
Ester value ............................... 40
Ester value after acetylation ................. 106

The oil contains some terpenes, and the following constituents; linalyl acetate, citronellyl acetate, a sesquiterpene ketone, termed doremone, doremyl acetate, cetyl alcohol and a dihydrosesquiterpene, ferulene, $C_{15}H_{26}$.

## Asafœtida

**Occurrence.**—This gum-resin is the product of several species of *Ferula*, probably chiefly of *F. scorodosma, F. narthex*, and, according to the British Pharmacopœia, *F. fœtida*. Asafœtida is largely imported from Bombay, to which place it is brought by the gatherers from Persia.

Asafœtida is extensively used in America in the treatment of a disease of horses known as "heaves." The gum-resin is also employed in small quantity as a flavouring agent, in sauces, etc.

**Chemical Constituents.**—According to Tschirch, the chief constituent of asafœtida is the *ferulic ester* of the alcohol *asaresinotannol*, $C_{24}H_{34}O_5$. This ester forms about 60% of the resin, besides which there are present traces of the free alcohol and free ferulic acid; 25% of gum; traces of vanillin; and up to 7% of an essential oil of complex nature.

**General Properties.**—Asafœtida occurs in tears separated or sticking together, but more often in large masses having a characteristic odour and taste. Externally it is either yellowish, violet, or brownish. The fresh fracture shows a white colour which changes gradually to a pink or violet and finally to a light yellowish-brown.

Tears of asafœtida are so scarce that were the consumers (chiefly veterinary surgeons) restricted to this form, the supply would be insufficient. The tears are much purer than asafœtida in mass, which is contaminated with much dirt and woody fibre.

**Commercial asafœtida** is said to be adulterated with cheaper resins, such as colophony, but the most common impurity is an abnormal proportion of mineral matter. Mörner and Fristedt examined a sample of asafœtida in tears, which contained 86% of mineral matter, consisting chiefly of calcium sulphate. J. Muter also described samples of asafœtida containing as much as 70% of stones. These no doubt had their origin in the practice, formerly much in vogue in the East, of packing drugs with as many heavy fragments of stone as could be got into the bale or cask.

So long as the ash does not exceed 15%, and the alcohol soluble substances are not below 50%, the sample is considered of fair quality.

The ash yielded by asafœtida does not afford an accurate criterion of the mineral matter of the sample, as the sulphur present exists, to a great extent, in organic combination and is fixed by the bases; whilst

a portion of the sulphate is liable to be reduced during ignition by the organic matter. Hence Mauch treats the sample with ten to fifteen times its weight of 60% chloral hydrate solution in water,[1] when the gum and resin slowly dissolve. The residue is washed on to an ashless filter-paper with chloral hydrate and then washed with alcohol, and after drying the residue is ignited and weighed.

W. A. Puckner (*Year-book Pharm.*, 1891, 211) found 5 samples of asafœtida to contain from 27 to 45% of their weight of matter soluble in 90% alcohol, while one other sample contained 59.5% of alcohol-soluble matter. The ash of the five samples ranged from 19.45 to 56.03%, the portion insoluble in hydrochloric acid varying from 1.37 to 21.96%.

From an examination of 11 samples of asafœtida, Martin and Moor (*Analyst*, 1900, **25**, 2) found the ash to range from 26.4 to 63.1%, and the ash insoluble in hydrochloric acid to range from 42 to 84% of the total, in one case the ash dissolved readily in hydrochloric acid with much effervescence, leaving only 3.6% insoluble. The proportion of the sample soluble in 90% alcohol ranged from 14.8 to 39.8% in twelve samples. (Similar figures have also been published by R. W. Moore, *J. Soc. Chem. Ind.*, 1899, **18**, 987; M. I. Wilbert, *Amer. J. Pharm.*, 1901, **73**, 131; and others.)

According to Hirschsohn, good samples of asafœtida should yield not less than 11% of soluble matter to petroleum spirit when the residue is dried at 17°, and not less than 6% of this residue should be lost on being heated to 120°. The use of these arbitrary temperatures is rendered necessary by the occurrence of volatile soluble constituents in asafœtida. Eleven samples of the gum-resin were found by Hirschsohn to give the following results by treatment with petroleum spirit.

Extract, dried at  17°.................... from 1.50 to 13.45%
Extract, dried at 120°.................... from 1.01 to  4.65%

Harrison and Self (*Year Book of Pharmacy*, 1912, 420) give a number of figures covering their examination of certain samples of asafœtida, and suggest that 1.5% of sulphur in the essential oil, expressed as a percentage of the actual gum resin present might be accepted as a minimum figure. These samples gave the following results:

[1] Whether by a "60% solution" is meant a mixture of 60 parts of chloral hydrate with 40 of water, or a solution of 60 grm. of chloral hydrate in 100 c.c. of water is uncertain.

| Nature | Loss on drying, % | Resin, % | Ash, % | Oil, % | Oil as percentage of gum resin | Sp. gr. of oil at 15.5° | Ref. index of oil at 20° | Rotation of oil (1 dcm.) | Percentage of sulphur in oil | Sulphur in oil as percentage of drug | Sulphur in oil as percentage of gum resin |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Mixed, chiefly soft paste | 22.3 | 50.1 | 4.3 | 17.7 | 18.5 | 0.929 | 1.5014 | − 0° 11′ | 22.3 | 3.95 | 4.13 |
| Soft paste | 26.0 | 41.3 | 3.6 | 8.3 | 8.3 | 0.943 | 1.5083 | −10° 20′ | 27.3 | 2.27 | 2.35 |
| Soft paste | 32.2 | 52.1 | 3.9 | 19.6 | 20.4 | 0.919 | 1.4968 | + 4° 13′ | 17.3 | 3.37 | 3.53 |
| Stiff paste | 24.4 | 23.9 | 43.7 | 5.5 | 9.8 | 0.964 | 1.5124 | − 9° 2′ | 21.7 | 1.19 | 2.13 |
| Soft mass | 18.7 | 20.9 | 52.6 | 5.9 | 12.4 | 0.973 | 1.5130 | −11° 43′ | 20.7 | 1.22 | 2.57 |
| Soft conglomerate | 24.0 | 56.8 | 2.7 | 13.9 | 14.3 | 0.973 | 1.5154 | − 9° 29′ | 23.6 | 3.28 | 3.37 |
| Drt conglomerate | 18.8 | 54.1 | 6.2 | 11.1 | 11.8 | 0.918 | 1.4951 | +10° 58′ | 17.1 | 1.90 | 2.02 |
| Hard mass, or "rock" | 7.9 | 19.4 | 46.1 | 4.6 | 8.5 | 0.993 | 1.5259 | − 8° 23′ | 31.4 | 1.44 | 2.67 |
| Large tears | 18.4 | 50.5 | 12.4 | 6.8 | 7.8 | 0.959 | 1.5089 | −10° 23′ | 21.1 | 1.43 | 1.65 |
| Tears | .... | .... | .... | 17.1 | .... | .... | 1.5078 | ........ | 17.5 | 2.99 | .... |
| Tears | .... | .... | .... | 20.8 | .... | .... | 1.5037 | ........ | 8.9 | 1.85 | .... |

Sechler and Becker (*Amer. Jour. Pharm.*, 1912, **84,** 4) give the following method of detecting ammoniacum and galbanum in asafœtida.

If 2 c.c. of a 1 in 10 aqueous emulsion of asafœtida diluted with 5 c.c. of water is floated on sodium hypobromite solution, an olive-green colour results. Galbanum emulsion gives a similar colour; but ammoniacum gives a cherry-red tint. Ammoniacum mixed with asafœtida gives a transient red colour. The reagent is prepared from sodium hydroxide, 20 grm.; bromine, 5 c.c.; water to 100 c.c. If 2 c.c. of asafœtida emulsion be floated on cold sulphuric acid no perceptible change occurs. Ammoniacum also gives no marked reaction. Galbanum gives a violet colour. On distilling off the essential oil, marked differences in appearance are noted. Oil of asafœtida is colourless and has a refractive index = 1.4974 at 20°. The gum resin yields about 4% of oil. Ammoniacum only yields 0.2% of dark yellow volatile oil which distils with difficulty; its ref. index is 1.4765 at 20°. Galbanum yields 20% of light yellow oil with the ref. index 1.4840. Consequently the presence of colour in the oil distilled from asafœtida should be regarded as suspicious. The ref. index should not fall below 1.496. The ref. index of a mixture of asafœtida and ammoniacum was 1.4959, that from asafœtida and galbanum 1.4929 at 20°.

In most cases, however, the ref. index of oil of asafœtida exceeds 1.5000.

The United States Customs Authorities recently laid down a limit for the "lead number" of genuine asafœtida. The method of estimating this figure is as follows:

Sufficient of the sample (about 20 grm.) is taken to furnish between 5 and 10 grm. of the resin. The alcohol-insoluble material is estimated in the usual manner. The first two filtrates, representing the major part of the sample, are transferred to a casserole, and the alcohol evaporated on the steam-bath. The resin is then dissolved in ether, filtered, transferred to a separator, and washed with water until the aqueous layer separates clear without any milkiness. The ether solution is filtered through a dry paper into a flask or beaker, and the solvent evaporated on the steam-bath.

Into a small tared beaker weigh roughly about 1.1 to 1.2 grm. of the resin prepared as above, and dry in the air-bath at 110° for 5 hours. Place in a desiccator, cool, and weigh. Dissolve in 20 c.c. of 95% alcohol, boiling gently until the resin is in solution. Transfer to a graduated 100 c.c. flask, washing the beaker with hot 95% alcohol, care being taken that the final volume does not exceed 70 c.c. Add 25 c.c. of the alcoholic lead acetate solution (described below), and allow to stand over night. Make up to the mark, filter through a fluted paper, and pipette into a beaker an aliquot part of 25 c.c., add 10 c.c. of water, and evaporate to 10 c.c.; add 5 c.c. of 10% sulphuric acid, and then 100 c.c. of alcohol, stirring vigorously to dissolve any separate resin. Filter off the lead sulphate on a tared Gooch crucible, and determine the lead in the usual way.

Carry out a blank on the alcoholic lead acetate solution, and calculate the amount of lead absorbed by 1 grm. of the dried resin. The number of milligrams of lead per gram is the lead number.

A food asafœtida should, according to the above authorities, have a lead number of at least 200.

The alcoholic lead acetate solution is thus prepared:

Dissolve 5 grm. of lead acetate in 20 c.c. of water, and add 80 c.c. of 95% alcohol. A turbidity generally results due to the precipitation of lead carbonate caused by the carbon dioxide contained in the alcohol. Leave over night. The clear supernatant liquid can then be used without filtration for the estimation of the lead number.

It will be seen that the "lead number" is thus a measure of the constituent (or constituents) of the ether-soluble portion of the resin, which forms a lead compound insoluble in alcohol. E. J. Parry (*Chemist and Druggist* 1913, **82,** 34), Rippetoe (*Amer. Jour. Pharm.*, 1913, **85,** 199) and Harrison and Self (*Pharm. Jour.*, 1913 [4], **36, 218**) have shown that this test is valueless.

The following table gives the acid and ester values of asafœtida according to several observers. The figures refer to the *extracted gum-resin*, with the exception of those obtained by K. Dieterich, which lose their meaning unless the ash is known:

| Character of sample | Acid value | Ester value | Observers |
|---------------------|------------|-------------|-----------|
| Extracted gum-resins......... | 27 to 55 | 145 to 182 | A. Kremel |
| Extracted gum-resins......... | 11 to 82 | 82 to 129 | E. Dieterich |
| Extracted gum-resins......... | 27 to 43 | 181 to 214 | Beckurts and Brüche |
| Commercial samples.......... | 65 to 80 | 80 to 130 | K. Dieterich |

According to Gregor and Bamberger, the methoxyl value of asafœtida ranges from 7 to 18.

**Tincture of asafœtida, B. P.,** is prepared by extracting 200 grm. of the gum-resin with 1 litre of 70% alcohol. The solubility of asafœtida in alcohol of this strength is sometimes more and sometimes less than its solubility in 90% alcohol, and since the gum-resin, as usually met with, rarely comes up to the pharmacopœial standard of alcohol-solubility, and resulting tincture will practically never contain the calculated standard of solid matter in solution. Thus, if 65% (the pharmacopœial standard) of asafœtida were soluble in 70% alcohol, the tincture should contain 13.0 grm. of extract per 100 c.c. Martin and Moor, however (*Analyst*, **25,** 3), found that the total solids from 7 samples of the tincture ranged from 4.3 to 8.5 grm. per 100 c.c. Tincture of asafœtida is therefore always much below its presumed strength, and the minimum amount of extract the tincture should contain should be specified. J. C. Umney (*Pharm. J.*, 1902, **69,** 492) considers 10 grm. of solids per 100 c.c. of tincture to be a reasonable standard. The sp. gr. of tincture of asafœtida ranges from 0.910 to 0.915 at 15.5°.

**Oil of asafœtida** is a liquid of disgusting odour, having a sp. gr. of about 0.975 to 0.990 at 15.5° and an optical rotation of about

$-10°$ in a 100 mm. tube. The oil was examined by Hlasiwetz in 1849, who stated that it was composed of *hexenyl sulphide* $(C_6H_{11})_2S$, and hexenyl disulphide $(C_6H_{11})_2S_2$, and was devoid of any oxygen or nitrogen. According to Brannt, asafœtida oil contains allyl sulphide and disulphide. Semmler, however, denied the accuracy of these results, and found the oil to contain pinene; a sesquiterpene having an odour resembling lavender; sulphur compounds having the composition $C_7H_{14}S_2$ (about 45%), $C_{10}H_{20}S_2$ (the constituent to which the oil owes its odour, about 20%), $C_8H_{16}S_2$, and $C_{10}H_{18}S_2$; and an oxygenated compound having the formula $(C_{10}H_{16}O)_n$, present to the extent of about 20%. This substance, on treatment with sodium, yields cadinene.

Oil of asafœtida has the following characters:

Sp. gr.............................. 0.915 to 0.993 at 15.5°
Opt. rot............................ $+11°$ to $-36°$
Rep. index......................... 1.4940 to 1.5260 at 20°

## ELEMI

**Occurrence.**—The name "Elemi" resin, is, in ordinary commerce, practically restricted to the somewhat plastic aromatic oleo-resin collected in the Phillippine Islands from several species of *Canarium* of which *Canarium luzonicium* is the most important. According to Dieterich the following resins are properly described as Elemi resin:

1. Manila elemi obtained from *Canarium species*
2. Yutican elemi obtained from *Amyris plumieri*
3. Mexican elemi obtained from *Amyris elemifera*
4. Rio elemi obtained from various resinous plants
5. African elemi obtained from *Protium heptaphyllum*
6. East Indian elemi obtained from *Canarium zephyrenum.*

**Chemical Composition.**—Manila elemi has been investigated by Tschirch and Cremer (*Arch. Pharm.*, 1902, **240,** 293), by Vesterberg (*Annalen*, 1887, 733: 1891, 615; 1892, 288; 1922, **428,** 243), and by Zinke and his pupils (Monatshefte, 1920, **41,** 253; 1921, **42,** 439). The principal constituent of the resin freed from its essential oil was found by Vesterberg to be an oxygenated substance to which he gave the name amyrin. This has been found to be a mixture of two isomeric triterpenic alcohols of the formula $C_{30}H_{49}OH$. There are also present $\alpha$- and $\beta$-elemic acids, $C_{37}H_{56}O_4$ and $C_{44}H_{80}O_4$, an amorphous resene, $C_{15}H_{80}O_1$, and a substance termed bryoidin $C_{21}H_{42}O_3$. Several other varieties of elemi have been investigated, principally

by Tschirch and his pupils, and all have been found to contain the two isomeric amyrins, which have also been discovered in the latex of numerous other plants.

Vesterberg describes the following method for the separation of the amyrins. Five hundred grm. of elemi resin are dissolved in 600 c.c. of 85% alcohol, on a water bath. After allowing the liquid to stand for two days, crude amyrin separates out in crystals. This is boiled with 200 c.c. of alcohol, filtered off and washed with a little hot alcohol, and finally dissolved in a very small quantity of hot 96% alcohol. Pure amyrin separates after standing. To separate the isomers 92 grm. of amyrin are heated with 100 c.c. of benzene, 61 grm. of benzoyl chloride and 39 grm. of pyridine on a water bath for an hour, and the mixture then evaporated to dryness. Pyridine is removed by neutralising with sulphuric acid, and then washing with water, then with alcohol, and then extracting with ether. The residue is recrystallised from petroleum spirit, and pure $\beta$-amyrin benzoate separates, melting at 230°. The residue from the ether, when recrystallised from petroleum spirit is pure $\alpha$-amyrin benzoate, melting at 192°. The alcohols are obtained by hydrolysis of the benzoates. Tschirch and Cremer prefer to separate the isomers by fractional crystallisation from acetone.

$\alpha$-amyrin melts at 183–184° and dissolves in hot cencentrated sulphuric acid to a yellow solution with a yellow fluorescence.

$\beta$-amyrin melts at 193–194° and gives a similar solution.

**Uses.**—Elemi is employed for special purposes in lithographic work, and it is also used to some extent in the varnish industry.

**Adulterants.**—This gum resin is often sophisticated with common turpentine and colophonium.

**General Properties.**—When fresh, elemi is a clear pale liquid consisting of resins dissolved in essential oil with a small amount of crystallised resins in suspension. On keeping, it changes to a soft crystalline yellow resin and sometimes becomes quite hard. All the elemis are softer than colophony, and can easily be cut with a knife. They have an odour like turpentine, and, in addition, a smell resembling aniseed, cloves, or lemon, according to the variety.

**Analytical Data.**—Dieterich has found for Manila elemis the following analytical figures:

Acid value 15 to 28
Ester value 6.1 to 35

Saponification value 25 to 60

Colophony and common turpentine when added increase the acid value.·

A resin having much in common with elemi is produced in Dominica, from *Bursera gummifera*, the so-called gommier tree.   It is used there for the preparation of torches and incense.   It has been sold on the London market as West Indian elemi.

Elemi resins from Southern Nigeria and from Uganda have also been exported and appear to be of excellent quality.   African elemi, reported upon by the chemists of the Imperial Institute (*Bulletin*, 1908, **6**; 252), was found to have the following characters:

|                              | 1       | 2       | 3       |
|------------------------------|---------|---------|---------|
| Ash.........................| 0.6%    | 0.53%   | 0.3%    |
| Acid value...................| 55.3    | 37.8    | 29.4    |
| Saponification value...........| 71.9    | 42.2    | 44.8    |
| Essential oil, %..............| 8.1     | 4.4     | 11.2    |
| Sp. gr. of oil at 15.5°.........| 0.8686  | ............ | 0.845 |
| Sp. rot. of oil................| +50.50  | ............ | +79.30 |

The essential oil of elemi is present to the extent of from 15 to 30% in the oleo-resin.   The principal constituent of the oil from Manila elemi is phellandrene.   The oil has the following characters:

> Sp. gr. at 15.5° ........... 0.870 to 0.915
> Opt. rot................. +30° to +55° (rarely +4° to +134°)
> Ref. index at 20°........ 1.4775 to 1.4900
> Acid value............... 0–2
> Ester value............. 4–10

Clover (*Amer. Chem. Jour.*, 1908, **39**, 613) has examined a large number of samples of the essential oil, obtained from various authentic elemi resins and found them to consist of the following groups.

(*a*)  Consisting almost entirely of *d*-limonene

(*b*)  Consisting of phellandrene, with some pinene or limonene

(*c*)  Consisting of terpinene or terpinolene

Semmler (*Ber.*, 1908, **41**, 1768, 1918, 2183, 2556) has isolated a phenol ether, elemicin, from the oil.   It is a liquid of specific gravity 1.063 at 20°, refractive index 1.5285, at 20°, and boils at 144–147° at 10 mm.   This substance is an allyl-trimethoxy-benzene.   Semmler and Siao (*Ber.*, 1916, **49**, 794) have also isolated a sesquiterpene alcohol from the oil which has a specific gravity 0.941 at 20°, optical rotation −5°, and refractive index 1.5030 at 20°.   It yields a sesquiterpene, elemene, on dehydration.

The essential oils obtained from less known elemis are interesting, but without any practical importance.

**Detection of Adulterants.**—Two tests have been put forward by P. Stoepel (*Apoth. Ztg.*, 1908, **23**, 440) for the detection of elemi and the identification of ordinary turpentine as an adulterant. When heated on a water-bath, elemi melts to a clear yellowish-green liquid, which is coloured eosin-red when dilute sulphuric acid (1:4) is added. Pure elemi when dissolved in absolute alcohol reacts neutral to blue litmus-paper, whereas when common turpentine is present the blue colour changes to red. When water is added to this alcoholic solution a pure white milky emulsion is obtained in the presence of pure elemi, whereas when turpentine is present a resinous brownish yellow flocky precipitate is thrown down.

## Galbanum

**Occurrence.**—This gum-resin is the product of *Peucedanum (Ferula) galbanifluum* and allied species of the *Umbelliferæ*.

**Chemical Composition.**—Galbanum usually contains about 9% of essential oil,[1] but the exceptional proportion of 22% has been recorded. In addition to essential oil, galbanum contains about 27% of gum and impurities, and about 64% of alcohol-soluble resin. This contains traces of free *umbelliferone* with about 20% of umbelliferone present as an ester of *galbanoresinotannol*, $C_{18}H_{29}O_2.OH$, a compound isomeric with the resin-alcohol of ammoniacum.

**General Properties.**—Galbanum is met with in grains, either loose or adhering *inter se* into a mass of a brown-yellow or often faintly green colour, and when fractured appears yellow to yellowish-white.

**Identification and Analytical Data.**—If finely powdered galbanum is boiled for a quarter of an hour with hydrochloric acid, filtered through a previously moistened filter-paper, and the clear filtrate carefully oversaturated with ammonia water, the resulting solution when seen by reflected light shows a blue fluorescence. When extracted with 95% alcohol not more than 50% of residue should be obtained.

The following table shows the analytical characters of galbanum as recorded by various observers:

| | | |
|---|---|---|
| Sp. gr. | ....... | 1.109 to 1.133 |
| Ash, % | ....... | 4.0 to 8.7 |
| Solubility in 96% alcohol = resin, % | 54; 74.2 | ............ |
| On the extracted resin { Acid Value | 19 to 40 | ............ |
| Ester Value | 63 to 95 | ............ |

[1] *Oil of galbanum* was included in the 1589 edition of the *Dispensatorium Noricum* and in the *Pharmacopœia Augustana* of 1580.

Galbanum resin yields from 12 to 24% of essential oil having the following characters:

Sp. gr. at 15.5°.............................. 0.905 to 0.955
Opt. rot.................................... −10° to +20°
Ref. index at 20°............................ 1.4840 to 1.4863

Semmler and Jonas (*Ber.*, 1914, **47**, 2068) have isolated from the oil, pinene (both the $\alpha$- and $\beta$-varieties), myrcene, a sesquiterpene, and a sesquiterpene alcohol, cadinol, $C_{15}H_{26}O$.

## Myrrh and Bdellium

**Occurrence.**—These closely allied substances are the oleo-resinous exudations from the stem of various species of *Balsamodendron* or *Commiphora*.

**Commercial Varieties.**—At least two distinct varieties of myrrh occur in commerce besides several of bdellium.  There is considerable confusion concerning the species of plants which yield true or *Herabol myrrh*, as distinguished from *Bisabol myrrh* and from *bdellium*.[1]  Herabol myrrh is probably derived from *Balsamea erythreum*.

Myrrh formerly came chiefly from Turkey, but now is collected principally in India, Arabia, and Somaliland.

As imported into the United Kingdom, myrrh consists of a mixture of true or Herabol myrrh with several allied products obtained from trees of the same genus (*Commiphora* or *Balsamodendron*).  These admixtures are picked out on arrival, so that the "gum myrrh elect" is nearly free from them.  The chief gum-resins imported in admixture with Herabol myrrh are opaque bdellium, African and Indian bdelliums, and Bisabol myrrh.

True or Herabol myrrh is a very fragrant gum-resin, varying in colour from yellow to dark red or even almost black.  It arrives in packages containing very mixed qualities, which are either purchased as such ("sorts") or are picked and graded into various qualities.  It occurs in small pieces varying in size from that of a pea to that of a chestnut.  It is employed to some extent in pharmacy, for the preparation of mouth-washes, in perfumery and for the manufacture of incense and similar fumigating materials.  In China the false or Bisabol myrrh is employed for the manufacture of joss sticks.

[1] The botany of the species yielding myrrh and bdellium has been exhaustively described by E. M. Holmes, *Pharm. Journ.*, 1898, **19**, 547; 1899, **26**, 77.

Myrrh contains from 2.5 to 8% of essential oil, from 50 to 60% of gum and from 25 to 40% of alchol-soluble resin. Traces of a bitter principle are present, and, usually, a small amount of mechanical impurities.

According to von Friedrichs (*Arch. Pharm.*, 1909, **245, 427**), the resin contains three resin acids soluble in ether which have been named $\alpha$-, $\beta$- and $\gamma$-commiphoric acids. The first two are isomeric having the formula $C_{14}H_{18}O_4$, whilst $\gamma$-commiphoric acid has the formula $C_{17}H_{22}O_5$.

There is also present a resin ester of commiphorinic acid, $C_{28}H_{35}O_8$. Two phenolic compounds were also isolated, $\alpha$-herabolmyrrhol, $C_{18}H_{26}O_5$, and $\beta$-herabolmyrrhol, $C_{20}H_{26}O_6$. A volatile alcohol, $C_{14}H_{22}O_2$, is present and an indifferent resene, $C_{42}H_{56}O_8$. Two resin acids not soluble in ether were also isolated, $\alpha$-myrrholic acid, $C_{15}H_{22}O_7$, and $\beta$-myrrholic acid, $C_{25}H_{32}O_6$.

The essential oil from true Herabol myrrh has the following characters:

| | |
|---|---|
| Sp. gr. at 15.5°............................ | 0.985 to 1.045 |
| Opt. rot................................... | $-30°$ to $-90°$ |
| Ref. index at 20°.......................... | 1.5180 to 1.5380 |
| Acid value................................ | 1 to 8 |
| Ester value................................ | 15 to 48 |
| Ester value (after acetylation)............... | 30 to 70 |

It is soluble, sometimes with slight turbidity, in 10 volumes of 80% alcohol.

Friedrichs has examined a sample of oil distilled from picked myrrh which had the following characters:

| | |
|---|---|
| Sp. gr. at 15.5°................................. | 1.011 |
| Opt. rot......................................... | $-73.80$ |
| Ref. index at 20°................................ | 1.5359 |
| Ester value...................................... | 47.6 |

He found *meta*-cresol, cumic aldehyde, cuminic aldehyde, and a sesquiterpene present. Traces of an acid, $C_{16}H_{21}O_3.COOH$, melting at 236°, were also found. Dipentene, pinene and eugenol have also been found in this oil.

Tucholka (*Arch. Pharm.*, **235,** 289) has examined the essential oil distilled from a Bisabol myrrh obtained from the interior of the Somatli country. It had a specific gravity 0.8836 at 15.5°, optical rotation $-14°$ 20', and boiling point 220°$-270°$. It was found to contain a hydrocarbon which the discoverer termed "bisabolene,"

and which is probably identical with the substance limene isolated by Burgess from oil of limes.

**Identification and Analytical Data.**—On treating true myrrh with nitric acid a violet coloration is produced. On this reaction various tests for myrrh have been based, some of which afford remarkable examples of badly devised and unsatisfactory applications. The subject has been investigated by H. G. Greenish (*Pharm. J.*, 1901, **67,** 666), who finds that the violet colour is yielded in the greatest intensity and purity by adding nitric acid to the ethereal or petroleum-spirit extract of the myrrh.[1]

The method of applying the test recommended by Greenish is to treat 0.5 grm. of the coarsely powdered sample of myrrh with 10 c.c. of ether, and shake at intervals during 10 minutes. 2 c.c. of the filtered liquid is evaporated at a gentle heat, and the capsule containing the residue inverted over another containing strong nitric acid, so that the residue may be exposed to the acid fumes. When thus treated, the residue from Herabol myrrh gradually acquires a violet colour.

Experiments made by A. R. Tankard, in A. H. Allen's laboratory, generaly confirmed Greenish's observations. The residue obtained on evaporating an alcoholic solution of myrrh gave the violet coloration very imperfectly; but by diluting the tincture with water and agitating the liquid with petroleum spirit, the substances to which the reaction was due passed into the latter,[1] and on separating and evaporating the petroleum spirit, the residue gave the reaction very dictinctly. Tankard prefers to moisten the residue with nitric acid (sp. gr. 1.42) instead of exposing it to the vapour of the acid. Bromine vapour gives the coloration distinctly when it is allowed to come in contact with an ethereal extract of true myrrh. Three samples of *Bisabol* myrrh examined by Greenish gave no˙ violet coloration with nitric acid, but readily responded to Tucholka's test for *Bisabol* (*vide infra*). *Bdellium, hotai,* and other allied gum-resins gave Greenish a negative result with the nitric acid test.

Old myrrh gives the nitric acid indication far less distinctly than fresh specimens, probably owing to volatilisation of the essential oil and oxidation of the resinous matters. In any case, the test only serves for the recognition of *Herabol* myrrh in presence of *Bisabol,*

[1] Greenish found the essential oil obtained by steam distillation of myrrh to give the reaction with great intensity, but the residue left in the distillation flask also gave the reaction, though he considered it possible that this might have been due to the incomplete volatilisation of the essential oil, since the fixed residue retained the odour of myrrh (and gave the violet coloration) after being kept for several weeks "on the top of the air-oven.".

*bdellium*, etc., and it is of no service for the detection of the latter gum-resins in admixture with true myrrh.

According to Tucholka (*Year-book Pharm.*, 1898, 180), a direct test for *Bisabol* myrrh consists in treating 6 drops of the solution of the sample in not less than 15 parts of petroleum spirit with 3 c.c. of glacial acetic acid, and then cautiously adding, without agitation, 3 c.c. of strong sulphuric acid. In the presence of *Bisabol* myrrh, a rose-red coloration is produced at the junction of the 2 strata, and the whole of the acetic acid layer shortly acquires a red colour which persists for some time. When *Herabol* myrrh is similarly treated only a slight rose coloration is communicated to the acid layer, and this does not increase, whilst the contact-line is first green, which changes to brown with a greenish fluorescence. The essential oil from *Bisabol* myrrh gives the rose-red colour reaction very distinctly.

Good samples of myrrh should contain not less than 30% of alcohol-soluble resin, and should leave not more than 8% of ash on ignition (many samples give not more than 4 to 5%). According to K. Dieterich, Herabol myrrh may yield as much as 50% to alcohol, whereas the proportion of resin in Bisabol myrrh is much smaller (sometimes 20%). E. Dieterich states the proportion of myrrh soluble in 96% alcohol at 23%, and the water-soluble constituents at 37 to 52%. These figures probably refer to Biasbol myrrh.

Tucholka found a sample of *Bisabol myrrh* to contain: gum soluble in water, 22.1; gum soluble in soda solution, 29.85; resin, 21.5; bitter principle, 1.5; essential oil, 7.8; water, 3.17; and inorganic and insoluble vegetable matters, 13.4%.

Bdellium, which closely resembles myrrh, and is often present in samples of myrrh, may be either African bdellium or East Indian bdellium. It is obtained from various species of *Commiphora* and *Balsamodendron*. It does not have the violet coloration with nitric acid or bromine that myrrh does. Dieterich gives the following figures for a number of samples of bdellium:

| | ACID VALUE | ESTER VALUE |
|---|---|---|
| African | 12.8 | 70 |
| African | 14.4 | 69.3 |
| African | 9.7 | 96.4 |
| African | 11.9 | 95.6 |
| African | 19.2 | 90.7 |
| African | 20.8 | 90.1 |
| Indian | 35.7 | 46.8 |
| Indian | 37.2 | 48.5 |

Hirschsohn states that myrrh should not contain more than 6% of matter soluble in petroleum spirit, any larger amount indicating adulteration.[1] He found the following proportions of matter soluble in petroleum spirit in samples of genuine bdellium:

| Origin | Dried at 17° | Dried at 120° |
|---|---|---|
| India.............................. | 13.37 | 11.29 |
| India.............................. | 16.57 | 9.87 |
| Africa............................. | 36.09 | 35.61 |
| Africa............................. | 35.68 | 34.79 |
| Africa............................. | 21.70 | 20.31 |

The presence of sulphur in the residue left after treatment of the sample with petroleum spirit is said by Hirschsohn to indicate the presence of *bdellium*, but this observation requires confirmation.

The following figures for myrrh and bdellium have been recorded by Kremel. The figures all refer to the resin extracted by alcohol, and not to the original gum-resin.

| | Sol. in alcohol, % | Acid value | Ester value | Sapon. value |
|---|---|---|---|---|
| *Myrrh:* | | | | |
|   Herabol................... | 39.5 | 64.0 | 95.0 | 159.0 |
|   Herabol................... | 42.0 | 60.2 | 116.5 | 176.7 |
|   Herabol................... | 23.9 | 70.3 | 145.8 | 216.1 |
|   Indian (? bisabol).......... | 30.7 | 42.1 | 130.8 | 172.9 |
| *Bdellium*.................... | 74.3 | 28.3 | 119.3 | 147.6 |

The following results were obtained by K. Dieterich on samples first thoroughly triturated with water, and thus the substance employed contained gummy matters, etc., as well as resin. The ester values were found by difference.

[1] This experience is strangely at variance with that of H. G. Greenish, who found a sample of genuine myrrh (previously mixed with twice its weight of sand) to yield 22.8 % to petroleum spirit (boiling under 80°), while the residue yielded 3.96, 3.72, and 2.55 %, respectively, to carbon disulphide, ether, and alcohol used successively.

For the estimation of the gum in myrrh, Mauch dissolves from 1 to 2 grm. of the sample in 15 grm. of a 60 % solution of chloral hydrate in water, and treats the filtered liquid by adding 100 grm. of strong alcohol. He obtained 75.2 % of gum by this method.

| Myrrh | Acid value | Ester value | Sapon. value | Soluble in alcohol, % |
|-------|-----------|-------------|--------------|------------------------|
| Herabol myrrh............... | 25.5 | 204.1 | 229.6 | 20 |
| Bisabol myrrh................ | 20.1 | 125.5 | 145.6 | 50 |

Two pure samples of Somaliland myrrh (*Ogo malmal and Guban malmal*) have been examined in the laboratories of the Imperial Institute (*Bull. Imp. Instit.*, 1914, **12**, 11). The results obtained are compared in the following table with those from commercial Aden and Somali myrrhs.

|  | Myrrh I. Ogo malmal | Myrrh II. Guban malmal | Commercial myrrh, Aden type | Commercial myrrh, Somali type |
|--|---------------------|------------------------|-----------------------------|-------------------------------|
|  | % | % | % | % |
| Moisture......................... | 10.2 | 10.5 | 8.9 | 12.9 |
| Ash.............................. | 3.0 | 5.2 | 18.0 | 4.4 |
| Volatile oil...................... | 13.8 | 11.8 | (not deter | mined). |
| Resin, soluble in alcohol.......... | 31.7 | 29.7 | 31.0 | 22.3 |
| Matter insoluble in alcohol........ | 54.5 | 58.5 | 60.1 | 64.8 |
| Consisting of: |  |  |  |  |
| Matter soluble in water (gum)....... | 52.1 | 56.8 | 36.2 | 58.6 |
| Matter insoluble in water (chiefly dirt)........................... | 2.4 | 1.7 | 23.9 | 6.2 |
| Acid value....................... | 26.5 | 17.8 | 19.0 | 40.5 |
| Saponification value.............. | 143.0 | 130.0 | 97.0 | 120.0 |

Gregor and Bamberger found a methoxyl value of about 13 for genuine myrrh.

**Tincture of myrrh,** is prepared by macerating 200 grm. of coarsely-powdered myrrh with a sufficient quantity of 90% alcohol, allowing the mixture to stand with frequent agitation for 7 days (3 days, United States Pharmacopœia), and making the volume finally up to 1000 c.c.

The direct distillation process is not directly available for the estimation of the alcohol in tincture of myrrh.

Thorpe and Holmes (*Proc. Chem. Soc.*, 1903, **19**, 13) have described the following distillation method for the estimation of ethyl alcohol in tinctures, essences, etc., containing essential oils and volatile substances such as ether, chloroform, camphor, etc. 25 c.c. of the tincture or other liquid, measured at 15.5°, is diluted with water in a separating funnel to about 100 or 150 c.c., and sufficient common

salt added to saturate the liquid. 50 to 80 c.c. of petroleum spirit (boiling below 60°) are now added, and the mixture shaken vigorously for 5 minutes. After allowing the liquids to stand for half an hour, the lower layer in the separating funnel is drawn off and extracted a second time with petroleum spirit, if necessary, after which it is placed in a distilling flask. The petroleum spirit extracts are washed successively with 25 c.c. of saturated brine, the washings being added to the main quantity of solution in the distilling flask. The liquid in the flask is neutralised if necessary and is then distilled, the distillate being made up to 100 c.c. and its sp. gr. determined as usual. The results obtained require a small correction, owing to the fact that the alcohol present in the tincture is diluted in the distillate to 4 times its original volume, and the errors of the alcohol tables are thus increased. The mean error of the tables at below 40% proof (for example, 0.972 sp. gr.) may be taken as +0.2% of proof spirit, and hence the percentage of proof spirit found by the above method requires a correction of 0.8%, which amount should be subtracted from the result obtained. The method is accurate and admits of very general application.

J. F. Liverseege (*Chem. and Druggist*, April 18, 1896) has described an indirect method for the estimation of the alcoholic strength of tincture of myrrh, which he considers preferable to any distillation process.

Great variations in the amounts of solids of tincture of myrrh have been observed (T. Macfarlane, *Canadian Bulletin*, No. 34), which are due to the variable amount of alcohol-soluble matters present in the gum-resin. Myrrh containing 30% of alcohol-soluble matter, of which only about 5% is volatile at 100°, should yield a tincture containing about 5.5 grm. of solids per 100 c.c. (C. G. Moor, "*Suggested Standards for Foods and Drugs*," page 193).

From the examination of a large number of commercial samples of tincture of myrrh by various observers, the sp. gr. at 15.5° was found to range from 0.848 to 0.856, the grm. of solids per 100 c.c. from 3.0 to 6.1, and the alcoholic strength from 82.7 to 86.8% by weight.

## Gamboge

Gamboge is a gum resin, obtained as an exudation from the cortex and bast of species of garcinia, principally *Garcinia Han-*

*buryi*, a tree growing in Siam, Cambodia and Cochin China; and *Garcinia Morella*, growing chiefly in India. It is found in commerce usually, in the form of yellow cylindrical rolls ("pipes"), or, more rarely, in lumps. The principal portion of the world's supply is produced in Siam. Gamboge is used to some extent as a pigment, and also as a drug, acting as an energetic cathartic.

It contains about 70–80% of resin, 15 to 20 per cent of gums and a small quantity of vegetable débris. The resin consists of several resin acids, which have been named "garcinolic acid," esters and a neutral resene. It should not contain more than 3% of ash and should be free from starch.

Pure gamboge should have the following characters:

| | |
|---|---|
| Acid value..................................... | 69–89 |
| Ester value.................................... | 43–67 |
| Saponification value............................. | 115–150 |
| Moisture...................................... | under 4% |
| Ash.......................................... | under 3% |

A garcinia resin is obtained from an unknown species of the tree in the federated Malay States. It belongs to the somewhat restricted class of oleoresins know as "natural varnishes." It is claimed to be equal in hardness to Japanese laquer. It has an acid value of 89.2 and an ester value of 3.3, and consists largely of resin acids.

### Frankincense

This important gum resin, also known as incense gum, is properly described as olibanum. It was known to the Greeks under the name Libanos, to the Romans as Olibanum, and to the Arabs as Loban, all of which names are derived from the Hebrew word *Sebonah*, meaning "milk."

It has from very early times been regarded as indespensable for the preparation of incense for religious ceremonial purposes.

There appear to be two varieties of frankincense known to the Arabs, who collect the gum resin, in, for example, the highlands of Abyssinia. Of these, one is termed Loban Dakar, or male frankincense; and the other Loban Maidi, or female frankincense. The trees yielding these two substances are *Boswellia carteri* and *B. frereara*. The former is found abundantly on the maritime limestone mountains South of Berbera in Western Somaliland, and thence eastward, whilst the latter is not found until the Habr Toljaela country is

reached, and is found farther west as far as the territory of the Warsangeli and Mijistain tribes.

The male frankincense appears to constitute the bulk of the frankincense of commerce, which is found on the market as tears, lumps, and siftings.

Olibanum contains from 5 to 10% of essential oil, about 60 to 70% of resin, and 20 to 30% of gum. The resin, extracted by alcohol, has the following characters (approximate).

```
Acid value....................................... 45 to 60
Ester value...................................... 40 to 60
Saponification value............................. 90 to 115
```

The resin consists of an acid, boswellic acid, both free and combined, and a resene, olibanoresene. The essential oil is a pale yellow liquid of balsamic odour having the following characters:

```
Sp. gr. at 15.5°............................ 0.875  to 0.885
Opt. rot................................... +15° to +30°
Ref. index at 20°.......................... 1.4725 to 1.4825
Acid value.................................    0 to 4
Ester value................................    5 to 20
Ester value (after acetylation)............   40 to 50
```

It contains pinene, dipentene, camphene and an alcoholic substance $C_{10}H_{16}O$, termed *olibanol*. Esters of borneol are also present.

### Sagapenum

Sagapenum is a gum-resin obtained from a species of *Ferula*. According to some authorities, it is the product of *Ferula Persica*, or, according to others, of *Ferula Szoritsiana*. Both plants are found freely in Persia and Arabia.

It occurs in masses of 5 to 10 lbs., dark brown in colour, with numerous white masses. It is brittle, but softens by the warmth of the hand. A small quantity of sagapenum occurs in commerce in the form of tears. These form yellowish or yellowish-red granules, somewhat resembling galbanum, but rather darker in colour. The tears, when fresh, are often greenish and opaque, but become yellowish and transparent on keeping. Sagapenum has an odour recalling that of garlic or asafœtida. The taste is bitter and acrid. Formerly the lump sagapenum was known as Persian and the tears as Levantine; but the latter may only refer to the route by which it reaches London.

Sagapenum contains from 50 to 60% of resin, from 20 to 30% of gums, and 3 to 11% of essential oil, together with small quantities of unimportant constituents.

The resin itself contains sagaresinotannol and umbelliferone.

Dieterich and Mauch have examined this substance and found the acid and ester values to be

| | 1 | 2 |
|---|---|---|
| Acid value | 13.96 | 14.81 |
| Ester value | 31.29 | 39.37 |
| Saponification value | 45.25 | 54.18 |

when estimated as follows:

One grm. is suffused with 30 c.c. of water and warmed for 15 minutes under a reflux condenser. Fifty c.c. of alcohol are then added and the whole boiled for 15 minutes. When cold, the liquid is titrated, with phenolphthalein as indicator. The saponification value is determined in the usual manner by boiling with alcoholic potash for 30 minutes.

When shaken with hydrochloric acid, its ethereal solution turns red-violet, due to the presence of umbelliferone. This reaction is also yielded by galbanum.

The following resinous substances may conveniently be included here.

### Ambergris

Ambergris is a pathological secretion in the intestines of the sperm whale which is sometimes found in the mammal itself, but is more often ejected and found floating on the sea or washed up on the shore.

According to J. Gattefossé (*Ga Parfumerie Moderne*, 1920, 259) the odorous constituents of ambergris exist already formed in certain cephalopods, such as *Elodone moschata*, upon which the sperm whale preys to a considerable extent. In normal circumstances, these substances as well as the crystalline ambrein, are expelled in the fæces. But if the whale be suffering from a certain micro-bacterial intestinal disease, these materials are not expelled. The lumps of ambergris are then formed, by the crystallisation of the ambrein and other matter, and are expelled fortuitously, or, if not, finally result in the animal's death. According to V. Hasslauer (*La Parfumerie Moderne*, 1921, 56) ambergris is a calculus formed in the whale by the undigested residues of its food, combined with

biliary and gastric juices, and, sometimes, fæcal matters. The calculus, when found in the interior of the animal, is not of so good quality, from the perfumer's point of view, as that which is expelled from the body. The sperm whale is very migratory, and goes far afield in search of food. The ambergris varies in character and quality according to the nature of the food consumed by the animal. Hasslauer considers that this influence is such that an expert can decide the part of the world from which a given specimen of ambergris has been obtained. Ambergris which has been expelled from the body and then exposed to the sun for several years is certainly the finest for perfume purposes.

Bauregard (*Less Cryptogames de l'ambre gris, Ann. de micrographie de Miquel* 1898) separated an organism which he named *Spirillus recti Physeteris*, from the intestines of the animal, which appears to be responsible for slowly attacking the fæcal matter and thus contributing to the formation of the calculus.

When the whale is suffering from the disease from the effects of which ambergris results, his recovery depends, in the main, on his ability to expel the secretion. If he is not able to do this he dies. Generally the dead body is eaten by fish, and the ambergris liberated, when it is either found floating on the surface of the water, or is washed ashore. If a sick whale is caught alive, the whalers will often make more out of the ambergris than out of the remainder of the carcase.

It is a highly valued and expensive perfume material and is used in the East as an aphrodisiac.

Its analysis is very indefinite, the perfumer being the best judge of its quality by its odour.

Pelletier and Caventou separated the odorous resin of ambergris and named it ambrein. Riban (*Comptes Rendus*, 1912, **154,** 1729: *Bull. Soc. Chim.*, 1912, IV, **11,** 754) re-examined ambrein and described it as a crystalline substance, melting, at 82°–86° and having the formula $C_{23}H_{40}O$.

A substance frequently collected and described as ambergris has been examined by H. I. Cole (*Philippine Journal of Science, through P. & E. O. R.* 1922, 300), and found closely to resemble the latex of *Artocarpus elastica*. True ambergris often contains fragments of horny gills of a species of cuttlefish, whereas a microscopic examination of the spurious ambergris usually reveals occluded fragments of

moss, leaves and bark, so that it is probably of vegetable origin. The chemical characters of ambergris are very variable, but such as have been recorded fall within the following limits.

M. p..................................... 60°–65°, softening at 40°–55°
M. p. of ether extract.................. 82°–88°
Sp. gr. at 15.5°........................ 0.780 to 0.925
Saponification value of ether extract...... 17 to 35
Iodine value of ether extract............ about 78

## Civet

Civet is a resinous material, conveniently classed with the oleo-resins. It is a glandular secretion of the civet cat, of which there are several species. It possesses an intense fæcal odour but is, when in very dilute solution, of the greatest value to perfumers, as it has valuable fixative properties, as well as an odour value when diluted.

It is a pale brownish mass of the consistency of butter, darkening on exposure to the air.

Genuine civet has the following characters:

Loss at 100° C............................. under 15 %
Ash........................................ under 2%
Soluble in acetone......................... 80 %–85 %
Acid number of petroleum spirit extract........ about 140
Sugar...................................... absent

The principal adulterants are gummy matters, banana pulp or other saccharine substances, and petroleum jelly. In the presence of gums or sugar, the petroleum spirit extract is reduced, and if petroleum or fatty oils are present, the acid values of the petroleum spirit extract are lowered.

To detect petroleum jelly in civet, 5 grm. are dissolved in 50 c.c. of acetone, care being taken that the substance is well disintegrated. The mixture is allowed to settle, and the clear liquid decanted. The residue is again treated with 50 c.c. of acetone, the liquid filtered, and the residue washed with acetone. When this is dried, it is greyish and powdery, but if petroleum jelly be present, it will be oily or pasty. In this event, the residue insoluble in acetone is extracted with petroleum spirit, when the petroleum hydrocarbons are dissolved out and can be weighed.

Schimmel & Co. (Bericht, 1924, 106) give the following figures for pure civet.

| | PER CENT. | ACID VALUE | ESTER VALUE |
|---|---|---|---|
| 1. Alcohol extract | 58 | 138.8 | 29 |
| 2. Ether extract (after 1) | 19.9 | 9.9 | 81 |
| 3. Chloroform extract (after 2) | 1.1 | ..... | .. |
| Residue | 7.5 | ..... | .. |
| Water | 13.5 | ..... | .. |

Nivière (*Bull. Soc. Chim.* 1920, 27, 794) has given an interesting account of an examination of samples of civet, which affords useful information in regard to adulteration. Four samples, described as pure were examined and gave the following results:

| | INSOLUBLE IN BENZENE | ASH IN INSOLUBLE PORTION |
|---|---|---|
| 1 | 6.6% | Traces |
| 2 | 6.4% | Traces |
| 3 | 7.0% | Traces |
| 4 | 18.35% | 18.15% |

The ash in No. 4 was talc.

After distillation of the benzene extract in a vacuum, the dissolved residues were redissolved in 96% alcohol. The amounts dissolved by alcohol, calculated on the original weight of the civet, were as follows:

| | |
|---|---|
| 1 | 56.7% |
| 2 | 57.01 |
| 3 | 55.21 |
| 4 | 38.82 |

The acid values of the alcoholic extract varied from 103 to 111, and the ester values from 15 to 25.

One of the samples (Mo. 2) was minutely examined. The portion insolutble in benzene melted at $58°-59°$, and had the following characters:

| | |
|---|---|
| Acid value | 8.4 |
| Ester value | 69.7 |
| Iodine value | 68.4 |
| Acetyl value | 80 |

Cholesterol was detected with certainty. From the alcoholic extract, the alcohol was removed *in vacuo*, and the residue dissolved in ten times its weight of benzene. The solution was at first clear, but soon began to deposit. The deposit was identified as glucose. The free acids in the benzene solution were removed by a 5%

solution of sodium carbonate, and from their odour appeared to be a mixture of caproic and caprylic acids. The sample was probably adulterated with wool fat and glucose.

Civet contains a small quantity of a volatile ketone, Zibethone, $C_{17}H_{30}O$. It melts at $32.5°$ and boils at about $345°-350°$.

## Castor

Castor is a much valued perfume material, and was at one time employed in medicine. It is now, however, but rarely employed as a drug.

It is the dried membranous follicles of the beaver, *Castor fiber*, situated between the anus and external organs of generation of both sexes, and not, as once believed, the dried testicles of the male. There are two pairs of glands attached to each animal, the lower ones being pear shaped and larger than the upper pair. They are filled with an oily, viscid and highly odorous substance, which, when fresh, is creamy white. When dried, it occurs as a brownish solid resinous mass, of characteristic odour. Two varieties are met with in commerce, the Canadian and the Russian, the former being the only one usually met with in this country.

Castor contains from 40 to 70% of resin, traces of an essential oil and from 4–5% of a crystalline substance known as castorin, with traces of benzoic acid and salicin. Mingand gives the following analysis of castor:

| | |
|---|---|
| Ether extract | 88.4% |
| Alcoholic extract (after ether) | 0.8% |
| Aqueous extract (after ether) | 0.1% |
| Acetic acid extract (after ether) | 0.6% |
| Volatile matter | 7.9% |
| Ash | 0.75% |

## Scammony Resin

"Scammony," as imported into this country, is a gum-resin obtained by incision from the living root of *Convolvulus scammonia*. It is much adulterated, often containing excess of mineral matter, chalk especially, or added starchy matter. The best samples may contain up to 90% of resin, but 70 to 85% is more usual.

Scammony resin is, for medicinal purposes, usually obtained by exhausting scammony root by alcohol, recovering most of the alco-

hol, and pouring the residual liquid into water and so precipitating the resin. After the resin has subsided it is collected on a filter, washed with boiling water and dried.

The root of Orizaba jalap, *Ipomœa orizabensis*, known also as Mexican scammony, yields a resin so similar to scammony resin that the British Pharmacopœia allows it to be used in medicine without distinction from true scammony resin.

The imported article is known in commerce as "virgin scammony" and, unlike the extracted resin, always contains an appreciable amount of ash. This rarely falls below 5%, and often rises to 12% in good commercial samples.

Starch is recognised microscopically, and by the iodine test.

Adulterating resins are detected by a comparison of the general characters of the samples (*see below*): colophony is detected by the high acid value and by the Storch-Morawski reaction.

Engelhardt and Schmidt (*Proceedings of the American Pharmaceutical Association*, 1910, **58**, 1027) have made an exhaustive examination of eight samples, whose origins were as follows:

1. Pure scammony from roots of *Convolvulus scammonia*
2. The purified resin extracted from (1) by alcohol
3. Pure resin extracted by the authors from the roots
4. Pure resin of *Ipomœœ orizabensis*
5 and 6. Probably pure gum-resins
7. Mexican scammony
8. The pure resin from (7) by alcohol.

From these samples they obtained the following results:

## (A) CHARACTERS

| No. | Moisture, % | Ash, % | Acid value | Saponification value | Ester value |
|---|---|---|---|---|---|
| 1 | 6.16 | 2.70 | 18.5 | 207.2 | 188.7 |
| 2 | 1.95 | .......... | 10.6 | 236.6 | 226 |
| 3 | 2.07 | 0.21 | 16.3 | 256.2 | 239.9 |
| 4 | 1.45 | 0.20 | 10.2 | 175.8 | 165.6 |
| 5 | 2.25 | 0.07 | 12.2 | 177.1 | 164.9 |
| 6 | 2.23 | 0.20 | 14.0 | 171.6 | 157.6 |
| 7 | 4.29 | 0.30 | 13.6 | 183.8 | 170.2 |
| 8 | 2.03 | 0.15 | 14.9 | 175.9 | 161 |

### (B) SOLUBILITIES

| No. | Pure ether (absolute) | Chloroform | Alcohol |
|---|---|---|---|
| 1 | 71.8% | 82.1% | 90.6% |
| 2 | 100.0 | 100.0 | 100.0 |
| 3 | 93.9 | 100.0 | 100.0 |
| 4 | 89.4 | 98.0 | 100.0 |
| 5 | 90.2 | 98.9 | 100.0 |
| 6 | 88.3 | 96.1 | 100.0 |
| 7 | 89.6 | 96.9 | 100.0 |
| 8 | 90.4 | 97.4 | 100.0 |

### (C) IODINE AND ROTATION VALUES

| | Iodine value | $[\alpha]_d$ in alcohol solution |
|---|---|---|
| 1 | 11.69 | $-25.98°$ |
| 2 | 10.45 | $-24.97°$ |
| 3 | 17.83 | $-24.24°$ |
| 4 | 11.60 | $-32.78°$ |
| 5 | 11.48 | $-33.8°$ |
| 6 | 13.93 | $-34.27°$ |
| 7 | 12.46 | $-31.31°$ |
| 8 | 11.65 | $-31.83°$ |

The specific rotations of colophony, mastic and sandarac are all positive, so that the rotation is reduced by these adulterants.

Taylor gives the following figures for true and Mexican scammony resins.

| | Acid value | Ester value | Iodine value |
|---|---|---|---|
| True resin...................... | 21.1 | 211.3 | 13.3 |
| True resin...................... | 15.5 | 222.5 | 10.8 |
| True resin...................... | 15.6 | 219.8 | 13.0 |
| True resin...................... | 18.2 | 221.7 | 14.3 |
| True resin...................... | 18.8 | 218.1 | 14.6 |
| Mexican resin.................. | 15.5 | 171.1 | 8.7 |
| Mexican resin.................. | 21.5 | 165.6 | 11.5 |

Both the true and Mexican resins are soluble in warm potassium hydroxide solution and are not precipitated on acidification, although the solution may be rendered turbid, on account of the natural presence of a small amount of fatty acids.

## Podophyllum Resin

Two varieties of podophyllum resin are known, and are used as purgatives in medicine.

The American variety is derived from *Podophyllum peltatum*, and the Indian variety from *Podophyllum emodi*.

The resin is extracted from the rhizomes by means of 95% alcohol.

Evans (*Analytical Notes*, 1911, **6**, 58) gives the following figures for three pure samples:

|  | P. peltatum | P. peltatum | P. emodi |
|---|---|---|---|
| Soluble in 90% alcohol.......... | 99.8% | 99.5% | ............ |
| Insoluble in 7% ammonia....... | 10.8% | 10.0% | ............ |
| Ash................................. | ............ | 0.5% | ............ |
| Acid value.,.................... | 174 | 145.6 | 110.1 |
| Ester value.................... | 95.5 | 119.0 | 95.8 |
| Saponification value............ | 269.5 | 264.6 | 205.9 |
| Iodine value.................. | 55.6 | 57.6 | 44.2 |

## Jalap Resin

Jalap resin is prepared by extracting the dried tubercles of *Ipomœa purga* with alcohol, recovering most of thea lcohol and pouring the residue into water and washing and drying the precipitated resin.

The portion of the resin insoluble in ether is known as jalapin.

Jalap resin consists in the main of two glucosidal resins known as jalapin (90%) and scammonin (10%). It is used in medicine as a powerful purgative. The resin should yield about 10% to ether and leave about 90% undissolved.

Its acid value varies between 13 and 27, and its ester value between 109 and 120 (according to Beckurts and Bruche), but according to Dieterich the ester value may rise to over 200.

This resin requires further examination.

# INDIA-RUBBER, GUTTA-PERCHA, BALATA AND ALLIED SUBSTANCES

By JOHN B. TUTTLE, B. Sc.

## POLYTERPENES

Under this heading are included substances having the same empirical composition as the terpenes, but whose fundamental molecules must be assumed to be multiples of $C_{10}H_{16}$.[1] The only examples of such compounds with which we have to deal are the fundamental hydrocarbons of india-rubber and gutta-percha; these are considered in the following pages.

## INDIA-RUBBER

**India-rubber** is obtained from the latex of trees, of many species, indigenous to tropical countries, more particularly to South America, Africa, Central America and Mexico. Certain of these species, particularly the *Hevea brasiliensis*, have been shown to be well adapted for cultivation, and extensive plantations are now in existence in Ceylon, the Malay Peninsula, Java, and other countries.

**India-rubber latex** is obtained from the trees by making incisions in the bark, and so laying open the *laticiferous vessels*. The latex exudes and is collected in various ways, according to the species, locality, etc. It forms an opaque liquid closely resembling animal milk in appearance, and, under the microscope, is seen to consist of an emulsion of globules, in a watery "serum." The globules consist of a substance which, when the latex is "coagulated" by suitable means and dried, becomes what we know as india rubber. Whether this transformation is of a "chemical" or merely of a "physical" nature is still undecided.[2] The average size of the globules is

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[1] Boswell, Hambleton, Parker and McLaughlin, *India Rubber Journal*, 1922, **64**, 981–5; Plummer and Burkard, *Ber.*, 1922, **55**, 3458–72. See discussions of these articles on page 365.

[2] See on this subject, Weber, *Ber.*, 1903, **36**, 3108; Eduardoff, *Gummi-Zeit.*, 1909, **23**, 809; Tuttle, *Ind. Rubber World*, 1923, **67**, 213–5; Loomis and Stumpff, *Ind. Rubber World*, 1923, **68**, 703–6.

different in different latices; globules of the latex from *Hevea brasiliensis* vary in diameter from $0.5\mu$ to $2\mu$,[1] whereas the average diameter of *Funtumia elastica* globules is only about $0.5\mu$.[2]

The sp. gr. of india-rubber latex is usually, but not invariably, below that of water; when freed from rubber the sp. gr. of the serum varies from 1.02 to 1.040. The rubber is accompanied in the latex by resins and by a number of other soluble and insoluble impurities.

**Analysis of India-rubber Latex.**—For the analysis of a rubber latex the following method may be adopted (D. Spence, *J. Inst. Comm. Research in Tropics*, 1907, **2**, 115): 100 grm. of the latex are coagulated, by means suited to the particular latex, and the rubber obtained is worked into the form of a thin sheet, and thoroughly digested with water, in order to remove soluble carbohydrates, organic acids, and inorganic salts. These soluble products may be estimated, if desired, by the method of dialysis described by Spence (*loc. cit.*). The washed rubber is then dried *in vacuo* until constant in weight. The dry rubber is cut up fine, and 5 grm. are extracted with acetone, at the b. p. of the latter; the amount of extract (resins and oils) is determined by direct weighing. The extracted rubber is dried *in vacuo*, and 1.5 grm. is then dissolved in chloroform in the cold. When homogeneous, the solution is heated to the b. p., centrifugalised to separate the mechanical impurities (Ditmar, *Gummi-Zeit.*, 1906, **20**, 364), filtered through a weighed filter of glass wool, covered with muslin, and the residue on the filter washed with chloroform, dried and weighed. The filtrate is evaporated to dryness in a weighed flask, dried in a rapid current of carbon dioxide, and then over sulphuric acid until constant in weight. *Nitrogen* is estimated in 20 c.c. of the original latex by Kjeldahl's method, and the *mineral constituents* (ash) by incinerating 20 c.c. of the latex. The results of the analysis may be expressed as in the following example, which represents a (somewhat abnormal) sample of *Funtumia elastica* latex. (D. Spence, *J. Inst. Comm. Research in Tropics*, 1907, **2**, 115; also 1907, **2**, 45 and 106.)

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[1] Victor Henri, *Compt. rend.*, 1907, **144**, 432.
   D. Spence (Ind. Rubber J., 1908, **36**, 233) gives $0.5\mu$ to $2.5\mu$; cf. also Bobiloff, *Archief voor de Rubbercultuur*, 1919, **3**, 374.
   Adriani (Pickles, *Brit. Assoc. Rep.*, 1906) gives 1/12250 in. as the average diameter.
[2] D. Spence, *loc. cit.*

Water .......................................... 76.2%
India-rubber.................................... 19.85%
Resins, etc. (soluble in acetone).................... 2.00%
Organic crystalloids (sugars, organic acids, and certain
    nitrogenous compounds)......................... 1.39%
Insoluble impurities (protein, etc.).................. 0.36%
Total nitrogen.................................. 0.438%
(Total nitrogen calcd. as protein................... 2.73%)
Mineral matter (ash), chiefly K, Fe, Ca, Mg as phos-
    phate, sulphate, and oxalate largely............... 0.266%

Girard and Lindet have recorded analyses of a number of india-rubber latices (*Bull. Soc. Chim.*, 1898, **19,** 812–815). In these instances the rubber was estimated by adding gradually an equal volume of 95% alcohol to the latex and stirring constantly, when the whole of the rubber collected on the surface of an amber-coloured mother-liquor.

| Source of latex | Sp. gr. | India-rubber, % |
|---|---|---|
| Pernambuco (*Hancornia*).................. | 0.990 | 31.6 |
| Africa (probably a *Liana* latex)............. | 0.987 | 33.4 |
| Parà (*Siphonia elastica*).................... | 0.986 | 42.6 |
| Nicaragua (*Castilloa elastica*)............... | 0.980 | 32.3 |
| Algiers (*Ficus macrophylla*) ............... | 1.000 | 37.5 |
| Algiers (*Ficus macrophylla*)................. | 1.005 | 37.1 |
| Algiers (*Ficus elastica*).................... | 1.001 | 17.3 |
| Algiers (*Ficus nitida*)..................... | 0.971 | 31.3 |
| Algiers (*Ficus levigata*)................... | 1.005 | 28.0 |
| New California (*Kickxia africana*).......... | 1.005 | 27.0 |
| Hevea Brasiliensis......................... | 0.9674 | 44.6 |
| Hevea Brasiliensis......................... | 0.9983 | 18.6 |

A modern source of rubber, not included among the latex-yielding species referred to above, is the Guayule shrub, *Parthenium argentatum*, A. Gray, the source of the so-called Guayule rubber. This shrub, which is indigenous to Mexico, is cut down and the rubber is obtained from it by various chemical and mechanical processes (see *Gummi-Zeit.*, 1908, **23,** 93–94).

*Rubber Latex.*—Largely owing to the work of Kaye (*India Rubber J.*, **64,** 435–42; 1922; *India Rubber World*, **68,** 418, 708, 1923); Hopkinson (*Ind. Eng. Chem.*, 1923, **15,** 1267–9), and Ditmar (*Chem. Ztg.* 1923, **47,** 711–2) a demand has been established for crude rubber

latex.   Precautions must be taken to prevent the coagulation of the latex before it is used; for this purpose ammonia is used almost exclusively.   This fact has a bearing on any analysis which may be made of preserved rubber latex.

The sampling of latex is of considerable importance.   The most important constituent is, of course, the crude rubber.   It has been observed that on standing there is a tendency for segregation to take place (O. de Vries, *India Rubber J.* **67**, 677, 1924), part of the crude rubber concentrating on the surface to form a sort of cream. The contents of a container of latex should be stirred vigorously before withdrawing a sample, and when this is not possible, small samples should be taken at varying depths in the container, and a composite sample prepared.

**India-rubber.**—The crude india-rubber of commerce is of very variable composition.   In addition to its fundamental constituent, the actual rubber hydrocarbon, it contains various impurities, some derived from the latex itself, others from extraneous sources.   These impurities consist of resins, carbohydrates, inositol, protein, colouring matters, tannins, mineral substances and water, which come under the first heading, and such "mechanical" impurities as bark, leaves, sand, clay, stones, etc., which belong to the second class. Plantation rubbers are largely free from the impurities of the second class.   This is particularly true of the grade "pale crepe;" many of the lots of smoked sheets contain appreciable quantities of bark, which must be removed by washing to make the rubber fit for certain uses.   Dark amber crepes, roll-brown crepe and similar low grades may contain large amounts of bark and dirt.   The plantation grades are also low in water content, and soluble impurities, but certain grades which are arriving on the market in more or less increasing quantities, may contain considerable amounts of water soluble substances, as, for example, those grades made from the whole latex, or prepared by the Hopkinson (*loc. cit.*) spray method. Still other grades, such as slab rubber, contain 10 to 15% of moisture in addition to a large percentage of the water-soluble constituents of the latex.

The essential constituent of crude india-rubber is the actual rubber substance, a hydrocarbon, having the molecular formula $(C_{10}H_{16})$(*cf.* page 365).   The name "polyprene" was formerly given to this hydrocarbon by Weber (see *Chemistry of India-rubber,*

London, 1902), on the assumption that it was a polymeride of isoprene $C_5H_8$. Harries (*Ber.*, 1904, **37**, 2706; 1905, **38**, 1195), however, believed that the hydrocarbon must be regarded rather as a polymeride of an eight-carbon ring compound 1:5 dimethyl *cyclo* octadiene (1:5).

$$\begin{array}{ccc} CH_3.C. & CH_2.CH_2. & CH \\ \parallel & & \parallel \\ CH.CH_2.CH_2.C.CH_3 \end{array}$$
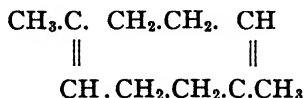
which is at present not definitely known (Pickles, *Trans. Chem. Soc.*, 1910, **97**, 1085 gives reasons for preferring the "open chain" formula $CH_2$. $CMe:CH.$ $[CH_2]_2.CMe:CH.[CH_2]_2.CMe:CH.[CH_2]_2$ to that of Harries).

Boswell, Hambleton, Parker and McLaughlin (*loc. cit.*) have come to the conclusion that rubber is really a polymer of isoprene, and that the formula should be $(C_5H_8)x$. Pummerer and Burkard also favour the $(C_5H_8)x$ formula. By hydrogenation of unvulcanised rubber, these authors have prepared $(C_5H_{10})x$, showing one double bond for each nucleus of $C_5H_8$. In view of this recent work, the processes for the production of synthetic rubber take on an added value, when we recall that the substances employed most largely have been butadiene $(C_4H_6)$, methylbutadiene or isoprene $(C_5H_8)$, and dimethylbutadiene $(C_6H_{10})$.

However one may be inclined toward either the $(C_5H_8)x$, or the $(C_{10}H_{16})x$ formula, from the analyst's point of view, no error is introduced, since it is well established that for each group of $C_5H_8$, there is one double bond, and for each group of $C_{10}H_{16}$, there are two double bonds. For our purpose, in view of the already established nomenclature for the estimation of rubber by the bromine method, as well as for other sufficient reasons, we propose to retain the older formula of $(C_{10}H_{16})x$, although it should be recognised that the later work is probably more accurate, and more nearly correct, than the older work of Weber, Harries, *et al.* An excellent review and discussion of this subject is given by Harry L. Fisher, *Ind. Eng. Chem.*, 1924, **16**, 627.

On exposure to light and air the rubber hydrocarbon absorbs oxygen, and is slowly converted into a brittle resinoid substance, $C_{30}H_{48}O_{10}[=(C_{10}H_{16})_3 + 5O_2]$, known as Spiller's resin (*J. Forts. d. Chem.*, 1865, 575). Crude rubber may, therefore, be expected to contain more or less of this substance. Crude rubber also contains,

in varying quantity, a substance which is insoluble in the ordinary solvents of india-rubber. This substance was described by Weber as an oxygen-containing compound of the composition $C_{30}H_{68}O_{10}$ $[= 3(C_{10}H_{16}) + 10H_2O]$, but Spence has shown (*J. Inst. Comm. Research in Tropics*, 1908, 3, 47–60, *cf*. Whitby, "Plantation Rubber," Chap. IV) that, at all events in the case of Para rubber, the purified substance contains nitrogen (about 5.4%), and is, at least in part, of protein nature. It is, however, extremely difficult to free the substance from the last traces of rubber hydrocarbon.

The amount of this protein substance is variously estimated at from 2 to 6%. Weber obtained 3.5%, but failed to detect the nitrogen present, and was therefore misled as to its true nature. Dekker (*Koll. Zeit.*, 1912, 11, 61) found 2.4% in fine Para, and 2.4 to 3.1% in plantation rubber. It is likely that the higher percentages reported are faulty, owing to including with the protein, (or insoluble matter) undissolved rubber.

Spence and Kratz (*Koll. Zeit.*, 1914, 14, 262) give the following method for the separation of insoluble matter from crude rubber: "100 grm. of washed and dried rubber are placed in 1 litre of benzine containing 0.3–0.5% of trichloracetic acid. If the rubber has been previously worked on the rolls it goes into solution more rapidly than otherwise. The solution is placed, if possible, in sunlight or is warmed on the water bath. As a rule, after twenty-four hours in sunlight, with repeated strong shaking, complete solution and disintegration of the rubber has occurred. The fine particles of insoluble material agglomerate and fall to the bottom. (Do not shake violently at this stage.) For the purpose of obtaining a sample of the insoluble material for examination, the upper liquid can be decanted, and the insoluble residue washed by two successive treatments of several hours each with a further quantity (500 c.c.) of acid-containing solvent. Filter; wash with benzine; powder in a mortar; wash with further solvent until no more traces of caoutchouc are extracted; wash with alcohol; dry. For the purpose of securing a quantitative separation, it is recommended to use centrifugation and filtration. In such cases it is better to make the original solution 2% instead of 10%.

The proportion of oxygen contained in commercial india-rubber is considered to afford a good criterion of the care with which the product has been collected, prepared, and stored.

The resins present in different crude rubbers differ greatly in their physical properties, and are, therefore, to some extent characteristic of the rubbers from which they are derived (*Cf.* Ditmar, *Die Analyes des Kautschuks*, etc., Vienna and Leipzig, 1909, pp. 170–173).

Raw, or unvulcanised, india-rubber is, at ordinary temperatures, soft, pliable, and elastic; when heated in boiling water or subjected to mechanical working, as between masticating rollers, it becomes still softer; below 0° it hardens and, in a large measure, loses its pliability. Freshly cut surfaces are easily welded together firmly by gentle pressure. Ordinary india-rubber begins to melt at about 120°. [Gladstone and Hibbert (*J. Chem. Soc.*, 1888, **53**, 686) state that purified india-rubber does not melt even at 200° in the absence of air, and that its solution in toluene retains its optical properties at that temperature.] After being melted it remains soft and adhesive on cooling; it hardens again when spread out in thin layers. On heating to 200° ordinary india-rubber is converted into a sticky mass which does not harden on cooling. The readiness with which these changes occur depends, to some extent, upon the source of the india-rubber. On dry distillation, india-rubber yields a variety of products, including *isoprene*, $C_5H_8$ (p. 424); *dipentene* or *caoutchene*, $C_{10}H_{16}$ (p. 434), and *heveene*, $C_{15}H_{24}$ or $C_{20}H_{32}$, a liquid with a faint smell and acrid taste, b. p. 315.[1]

The odour of crude india-rubber (which is really that of its impurities), is characteristic, and in many cases affords a clue to its origin.

India-rubber is insoluble in water, but is capable of absorbing up to 25% of its own weight of that liquid, and is somewhat hygroscopic. Though it can hardly be said to dissolve, in the ordinary sense, the unvulcanised rubber forms a solution with chloroform, benzene, toluene, the various petroleum and shale distillates, carbon tetrachloride, carbon disulphide, etc. Similar solutions are formed with the various fatty and essential oils, fused naphthalene, phenol, etc. Although india-rubber is insoluble in absolute alcohol, the viscosity of a solution in carbon disulphide is much decreased by the addition of alcohol to the extent of 10% of the weight of carbon disulphide; such a solution, on account of its low viscosity, is often very convenient to work with. The viscosity of a rubber solution varies considerably with the solvent employed, and also with the

[1] For a complete account of the products of destructive distillation see Pickles, B. A. Report, 1906.

kind of rubber, and with the amount of mechanical working to which it has been subjected. It is stated that the viscosity bears some intimate relationship to the degree of polymerisation of the molecule, and thus to the "quality" of the rubber (Schidrowitz and Goldsbrough, *J. Soc. Chem. Ind.*, 1909, **28**, 3–6). The readiness with which india-rubber passes into solution increases with the amount of working (mastication) it has received.

India-rubber is a non-conductor of electricity and becomes strongly electrified when rubbed.

The sp. gr. of highly purified rubber is 0.911 at 17°; that of the technically pure substance varies from about 0.915 to about 0.931:

The india-rubber hydrocarbon, being an unsaturated compound, is very open to attack by the halogens, chlorine and bromine, additive compounds being formed in the first instance. This property of combining additively with bromine, in the proportions represented by the formula, $C_{10}H_{16}Br_4$, has been made use of by Budde, (*Pharm. Zeit.*, 1905, **50**, part 32) who has devised a process for the direct estimation of pure rubber in raw rubber. This process has been subjected to criticism by Harries and Rimpel (*Gummi-Zeit.*, 1909, **23**, 1370–1371) and others.

Ozone also forms an additive compound with india-rubber; the ozonide is a viscid oil, which solidifies to a glassy, explosive solid of the composition $C_{10}H_{16}O_6$. This substance is readily hydrolysed by distillation with steam, yielding lævulic aldehyde, lævulic acid, and lævulic aldehyde peroxide. (Harries, *Ber.*, 1904, **37**, 2708; 1905, **38**, 1195.)

Mention has already been made of the hydrogen addition product, $(C_5H_{10})x$ of Pummerer and Burkard.

Strong sulphuric acid chars and oxidises india-rubber on heating, and nitric acid converts it into a substance of a yellow colour, which on prolonged boiling yields oxalic, camphoric, camphoronic acids, and other products. The oxides of nitrogen react readily with india-rubber, yielding, under certain conditions, definite products. The action of the halogens, oxides of nitrogen, and vulcanising agents (*cf.* p. 374 *et seq.*) on india-rubber, and the products obtained are fully discussed by Caspari (*J. Soc. Chem. Ind.*, 1905, **24**, 1274).

**Analysis of Raw India-rubber.**—In the analysis of raw rubber Weber recommends the estimation of the loss on washing, oily and resinous matters, combined oxygen, and mineral matter, pure india-

rubber being estimated by difference. The method of procedure is as follows:

**Loss on washing** is estimated on as large a sample as possible,[1] preferably between "washing-rolls" in a stream of water, the rubber being afterwards carefully dried before weighing. The figure obtained represents water, bark, and other plant tissues, sand, soluble impurities, organic and inorganic, etc. Speaking broadly, the loss on washing is in no way an indication of the quality of the crude rubber, but its amount naturally influences the cost of the purified raw rubber when ready for manufacture. For these reasons, to estimate the loss on washing, the crude product should be treated as nearly as possible in the same way as it would be by the manufacturer in preparing it for use in the factory.

**Oily and resinous matters** may be estimated by extracting 2 to 5 grm. of the finely-divided, washed rubber, dried *in vacuo* or in a current of carbon dioxide, with acetone, in a Cottle[2] or similar extraction apparatus. Various forms of extraction apparatus have been devised for rubber extractions and similar purposes. Those forms are preferable in which the vessel containing the sample, in contact with the solvent, is continuously surrounded by the hot vapours of the solvent, this arragement enabling the extraction to be carried out at the boiling point of the solvent employed. The time required for extraction should be 8 hours.[3] The acetone is distilled from the flask, the resinous residue in the flask is dried at 100°, and its weight calculated as a percentage on the washed dry rubber. The figures published by different workers for the resin

[1] The question of sampling is of prime importance if the results of this test are to be of any value. This is particularly true of the wild rubbers, and it is to be noted that it is chiefly in the examination of such rubbers that this test is intended to be used.

[2] This extractor was designed by Cottle, but owing to its adoption and use by the Underwriters' Laboratories at Chicago, has become better known in the literature as the "Underwriters' Extractor." It has been the basis for the development of the U. S. Bureau of Standards, the Joint Rubber Insulation Committee, and other extractors used in rubber analysis.

[3] Eight hours should suffice for any properly prepared sample extracted under exact conditions. However, some uncured samples may fuse together into a solid mass, and require a longer time for comparatively complete extraction. In such cases, extract until the solution in the extraction cup is colourless, and continue for four hours longer. Uncured samples should be sheeted thin and rolled between hardened filter paper, to effect a thorough and more rapid extraction. The expression "complete extraction" is a misnomer; additional quantities of the extract can be dissolved up to 48 hours, or even more, but the amount so obtained is but a small proportion of the total, and is more or less constant. Hence, if we interrupt the extraction at a definite point, we secure results which serve the purpose of indicating the quality of the rubber, and are comparable with other extracts made in a similar manner. The same is true to a large extent with the chloroform and alcoholic potassium hydroxide extractions, and we really deal with comparable rather than with absolute values. The necessity for continuous extraction is explained on the same basis; with samples of approximately the same degree of fineness the extraction is a matter of time, rather than the number of times the syphon empties; hence, standing overnight would permit the solvent to extract a considerable quantity of soluble matter that otherwise would not be extracted. Many of the variations in check results are really due to faulty manipulation, rather than to the type of extractor or to the fineness of the sample.

content of various rubbers are by no means in agreement. Thus while, in the following table, Para rubber is shown as containing only 1.2 to 1.3% of resins, Tankard[1] found in washed, dried Para 2.83%, and this is not an unusual figure to obtain. The following results were published, respectively, by H. L. Terry,[2] C. O. Weber,[3] and R. Henriques.[4] Henriques' figures were apparently obtained by

| Variety of rubber | Resin, % | | |
|---|---|---|---|
| | Terry | Weber | Henriques |
| Para........................... | 1.2 | 1.3 | 1.3 |
| Mozambique..................... | 3.0 | 3.2 | 3.8 |
| Sierra Leone, red................ | 7.4 | 9.7 | 5.8 |
| Assam........................... | 9.3 | 11.3 | 11.3 |
| African ball..................... | 22.8 | 26.1 | ........... |
| African flake.................... | 41.2 | 63.9 | ........... |

extraction with acetone. Terry's results were obtained by extracting the finely cut rubber for several hours in a Soxhlet apparatus with alcohol. The Para figures in this table are undoubtedly too low; 3.5% would be nearer the correct amount. First grades of plantation rubbers give 2.5–3.0% extractable resins.

In the case of certain rubbers, which contain resins similar in character to the alban of gutta-percha (p. 418), the use of glacial acetic acid for extracting the resins, which are very sparingly soluble in acetone, has been recommended. Sierra Leone rubber is a case in point.

The *combined oxygen* is estimated, according to Weber, by carrying out a combustion of the washed, dried, acetone-extracted sample (dried, after acetone extraction, in a current of oxygen-free gas). The oxygen is taken as the difference between the weight of the original sample and the combined weights of carbon, hydrogen, and ash estimated by combustion. By this method Weber found 1.2 to 7.4% of oxygen in various brands of rubber (ash-free). It should be noted, however, that this method takes no account of the nitrogen present in the raw rubber in the form of protein (see p. 372).

[1] Allen's Comm. Org. Analysis, 1907, Vol. 2, Pt. 3, p. 290, footnote.
[2] *J. Soc. Chem. Ind.*, 1889, **8**, 173.
[3] *J. Soc. Chem. Ind.*, 1894, **13**, 477.
[4] Der Kautschuk und seine Quellen, Dresden, 1899, Table I.

The *mineral matter* is estimated by incinerating not less than 1 grm. of the washed, dried rubber. The ash of different brands varies considerably in quantity from about 0.3% in the case of fine Para, upwards, and the composition of the ash is to some extent characteristic of the raw rubber from which it is derived (Weber, Chemistry of India Rubber, 1902, pp. 12–13. Spence, *J. Inst. Comm. Research in Tropics*, 1907, **2**, 113).

As the result of a study and comparison of various methods (enumerated in *J. Inst. Comm. Research in Tropics*, 1907, **2**, 94, footnote 6) proposed for the complete analysis of a sample of raw rubber, Spence has suggested the following scheme as a standard method (*J. Inst. Comm. Research in Tropics*, 1907, Reprints, No. 10).

**Sampling.**—Great care must be exercised in selecting the sample. At least 500 grm. should be taken from the bulk, and this should be made representative of the various biscuits, balls, etc., of which the bulk is composed. On this sample the *loss on washing* is estimated as above described.

**Estimation of Resins, Etc.**—About 5 grm. of the washed, dry sample are weighed out, cut up very finely and extracted with acetone for 8 hours. Dry the extract to constant weight at 90°.

In rapid work the partially dried sample may be extracted at once with acetone, and the amount of moisture present may be taken as the difference between the weight of the dried extract and that of the dried rubbery residue.

**Estimation of India-rubber.**—1.5 grm. of the dry, extracted rubber is dissolved in about 100 c.c. of benzene at ordinary temperature in a flask which can be shaken vigorously at intervals to hasten solution. *Hevea* rubber dissolves very slowly, whereas the poorer classes of rubber all dissolve readily within 6 to 8 hours. The solution is made up with benzene to 200 c.c. in a graduated flask, is well shaken, and is then filtered through a previously weighed funnel, provided with a tightly-fitting plug of glass-wool. 100 c.c. (or less if filtration prove to be unduly slow) of the filtrate are collected in a graduated flask, and the remainder of the solution is then diluted with benzene, filtered, the residue on the filter (consisting of insoluble impurities) well washed with benzene and finally with alcohol, dried at 65° and finally *in vacuo* over sulphuric acid, until constant in weight. The amount of *insoluble impurities* thus arrived at includes the insoluble substance referred to on p. 382. The 100 c.c.

of benzene solution is transferred to a weighed Erlenmeyer flask, the benzene is distilled off, the last traces in a current of carbon dioxide, and the flask is dried *in vacuo* over paraffin wax and sulphuric acid until constant in weight. The increase in weight represents the amount of pure rubber in the sample.

**Nitrogen** is estimated in the washed, dry sample by Kjeldahl's method. Whether it is legitimate to use the factor 6.25 and call the product protein is doubtful. It is certainly not so in the case of unwashed rubber, in which nitrogen is present in other forms than that of protein.[1]

**Mineral matter** is estimated in 5 grm. of the sample, by incineration in a platinum or porcelain crucible. The presence of the following constituents should be looked for: iron, aluminium, calcium, magnesium, chlorides, sulphates, and phosphates, as these may give some clue to the source of the sample (*cf.* p. 379).

The results of an analysis should be expressed as percentages on the washed and dried sample. Such results of analysis are not sufficient in themselves to permit of a full valuation of the rubber sample, and various suggestions have been made for supplementing the chemical analysis by physical tests—of tensile strength, resiliency, viscosity of solutions, etc. Agreement has not, however, been arrived at on this subject.[2]

**Rubber Latex.**—There are very little data as yet on the analysis of preserved rubber latex. The principal constituents are crude rubber, ammonia, water-soluble content, acetone-soluble resins, proteins and ash.

*Crude Rubber.*—Place 10 grm. of latex in a nickel or porcelain dish, and dry to constant weight at 100°. This is really the total solids, but the estimation is made in this manner since much of the latex is used in this form.

*Ammonia.*—Take 10 to 20 grm. of latex, and 50 c.c. $N/10$ NaOH and distil the ammonia into a standardised $H_2SO_4$ solution. Titrate the excess acid and calculate to percentage.

*Water-soluble.*—Take the residue from the crude rubber estimation, add 100 c.c. of water, boil 2 hours, decant and wash with boiling water. Dry the rubber to constant weight at 100°. The loss is the water-soluble matter.

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[1] Spence. This is particularly true of preserved latex, and rubber derived therefrom.
[2] For information on these points, the reader should refer to Schidrowitz, *Ind.-rubber J.*, 1909, 37, 313, 381, 521.

*Resins.*—Make the usual extraction with acetone, using the dried sample from the estimation of water-soluble constituents.

*Proteins.*—Estimate the nitrogen in a dried sample by the Kjeldahl method. Use the factor 6.25, although this is doubtless low, and the results will be only a fair approximation of the truth.

*Ash.*—Ignite the residue from the estimation of the resins.

**Analysis of Unvulcanised Rubber Mixings.**—This is carried out in general on the same lines as that of vulcanised samples.

The difficulty attending the application of the alcoholic sodium hydroxide process for the estimation of fatty substitutes (p. 383) to unvulcanised samples consisting of soft rubber and substitutes, is overcome by Henriques in the following manner: 5 grm. of the sample are heated for 1 hour with 25 c.c. of benzene, in a flask fitted with reflux condenser, and the flask and contents are allowed to stand overnight. 25 c.c. of N alkali are added, and the boiling is repeated for 4 hours. The solvents are driven off on a water-bath, and the residue rinsed into a large basin with hot water. The mass is extracted several times with boiling water, the alkaline washings being poured off, and the residual rubber is kneaded in water and extracted until the washings are no longer alkaline; it is then dried at 100° and weighed, the loss in weight representing the fatty substitute present.

The principal objection to this procedure is the danger of the occlusion of alkali, it being extremely difficult to remove all of the alkali from the rubber by washing, and at best, the process is long and tedious. The following modification has been suggested, and has merit:

5 grm. of rubber are dissolved in 25 c.c. of benzene (or more, if the solution is too viscous). Add 25 c.c. of N/1 alcoholic potassium hydroxide and boil for 4 hours. Transfer to a separatory funnel, add 100 c.c. of water, shake thoroughly, and draw off the aqueous layer. Wash with several portions of 25 c.c. of water, and unite the washings with the first fraction. Evaporate to dryness, take up in boiling water, transfer to a separatory funnel, cool, add sufficient hydrochloric acid to neutralise the alkali and soaps present (methyl orange is a satisfactory indicator) and extract the fatty acids with ether. The united ethereal fractions are washed with distilled water, transferred to a tared beaker or flask, the ether distilled and the residue dried at 90° and weighed.

**Vulcanised India-rubber.**—When heated with sulphur or sub-jected to the action of chloride of sulphur ($S_2Cl_2$) at ordinary tempera-tures, india-rubber undergoes a remarkable change in properties. The product of these reactions, which is known as "vulcanised rubber,"[1] represents the form in which india-rubber almost invariably comes into use, there being but few purposes for which raw or unvul-canised rubber can be employed, for which the vulcanised product is not more suitable. The degree of sulphuration attained is depend-ent, in any given case, on the temperature and time allowed for the process, on the proportion of sulphur employed, and on the com-position of the rubber compound. Sulphur "carriers"[2] are largely employed for accelerating and facilitating vulcanisation. Those in most common use are antimony pentasulphide, litharge, white lead, basic sulphate of lead, lead thiosulphate, lime, and magnesium oxide and carbonate.

The past decade has seen the development, on an enormous scale, of the use of organic substances as "sulphur carriers" or "acceler-ators" of the vulcanisation process. These are usually basic com-pounds containing nitrogen. The most commonly used are aniline, hexamethylenetetramine, thiocarbanilide, di- and tri-phenyl guani-dine, $p$-nitrosodimethylaniline, ethylidine aniline, etc. We have also the group of substances, known as the "ultra-accelerators" on account of the extreme speed which they give to the vulcanisa-tion reaction, the best known being the thiocarbamates, made by the interaction of carbon disulphide and a secondary amine (such as dimethylamine); the thiuram disulphides, and the piperdine-carbon disulphide reaction product.

From the analyst's point of view, it is unfortunate that very little work has been published on the identification of organic accelerators. Not the least of the difficulties attending the attempt

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[1] Vulcanised rubber was originally applied to the product resulting from heating rubber and sulphur, with or without other substances. Today we extend the definition to include the chemical combination of rubber with any element or group of elements to form a new substance having new physical properties which are desirable from a commercial view-point. Thus we accentuate the production of new physical properties, rather than the chemical combination of rubber with a single element such as sulphur.

A hard rubber, or ebonite, obtained by heating rubber and sulphur, and articles such as bathing caps, surgeon's gloves, etc., obtained by the treatment, at ordinary temperatures, of rubber with sulphur chloride, are both vulcanised rubber, although they have no phy-sical properties in common. According to this definition, therefore, the use of any other means than the commonly employed sulphur or sulphur chloride would produce "vulcan-isation" if the product possessed desirable physical properties.

On the subject of vulcanisation, see *J. Soc. Chem. Ind.*, 1894, **13**, 11, 473;1895, **14**, 436; 1902, **21**, 712; *Chem. Zeit.*, 1894, **18**, 701; 1895, **19**, 235, 382, 1918;*Gummi-Zeit.*, 1900, **14**, 17, 33; 1902, **16**, 561-564; 1910, **24**, 1211.

[2] The term "accelerators" is commonly used today to cover all such sulphur carriers whether or not they are organ in ciororganic substances.

to identify organic accelerators is the very small amount of these substances necessary to produce vulcanisation. This is especially true of the ultra-accelerators, when the amounts used seldom exceed 0.1 to 0.2% of the amount of the rubber present.

In Parkes' cold process, the articles to be vulcanised are immersed in a solution of 2.5 parts of sulphur chloride ($S_2Cl_2$) in 100 parts of carbon disulphide, or benzene, or, in the case of waterproof fabrics, the surface of the material is moistened with the solution. The sulphur chloride used should be as nearly as possible pure $S_2Cl_2$; it should, in particular, be free from excess of chlorine, the presence of which gives rise to a brittle product on vulcanisation. The action in Parkes' process is held by C. A. Burghardt to consist in the substitution of sulphur for a portion of the hydrogen of the rubber hydrocarbon, hydrogen chloride being simultaneously formed. Weber, however, regards the process as one of simple addition, and postulates a series of chlorosulphides analogous to the sulphides of hot vulcanisation.[1] India-rubber vulcanised by Parkes' process ("cold cured" rubber) always contains both chlorine and sulphur.

Pure "hot-vulcanised" india-rubber is of a greyish colour and is not appreciably adhesive at cut surfaces. It remains elastic and pliable down to fairly low temperatures. Vulcanised rubber absorbs an appreciable quantity of water and only swells up, without dissolving, in the ordinary solvents of india-rubber. It slowly absorbs atmospheric oxygen, and in an atmosphere of carbon dioxide takes up about its own volume of the gas. Vulcanised rubber usually contains a portion of its sulphur in the free state. This can be partly removed by boiling the rubber with sodium hydroxide solution, a treatment which sometimes is used in preparing "non-blooming" articles.

**Analysis of Vulcanised India-rubber.**—The insolubility of vulcanised rubber in ordinary solvents renders inapplicable to its analysis the processes employed in the case of raw rubber. The complete analysis of a complex india-rubber article by physical and chemical tests is a very tedious operation. Fortunately, it is rarely required.

As is well known, india rubber goods are rarely manufactured from india-rubber only, and generally contain one or more of the following substances in admixture: mineral matters, rubber substitutes or surrogates (vulcanised, oxidised, or polymerised oils),

[1] *Chem. of Ind.-R.*, 1902, p. 97 *et seq.*

reclaimed rubber, ground waste rubber, bituminous substances (asphalt, pitch, M.R., etc.), resins, rosin oil, fatty and mineral oils, albumin and paraffin-wax.

There are many difficulties to be overcome in the analysis of vulcanised rubber. Substances added to the rubber before vulcanisation are liable to undergo chemical changes when heated in presence of sulphur; and, since the analysis of rubber resolves itself into the recognition and estimation of the substances originally mixed together, the problem presented is of far greater complexity even than that of the proximate analysis of the finished article.

The difficulty of obtaining a homogeneous sample of manufactured rubber is sometimes considerably, though careful, modern, large-scale manufacture tends continually to minimise this difficulty. Fairly large quantities of the substance should be taken and reduced, by cutting, rasping, or other suitable means, to a very fine state of division.

The *sp. gr.* of india-rubber is of little or no value in judging of its purity or quality. Samples which float on water are usually free from any notable admixture of mineral matters, but the test is not absolute, as manufactured rubber frequently contains air vesicles.

The *apparent sp. gr.*, or what might be called the *mass sp. gr.*, is determined on a single piece of some size, say not less than 5 grm. The ordinary balance may be used, weighing in air and in water; or we may use a Jolly balance.

The *real sp. gr.* is determined by means of the sp. gr. bottle. As much as practicable of the finely divided sample is placed in the bottle together with some distilled water, the bottle is attached to an air-pump, the occluded air removed by exhaustion, and the bottle then filled up with air-free distilled water. To obtain the rubber in a sufficiently fine state of division, a pair of laboratory mixing rollers should be used or the sample should be rasped. The latter method is quite successful, provided the rubber contains an appreciable amount of mineral matter.

From these two sp. grs. a number $(p)$, representing the porosity ("microporosity") of the samples may be deduced by the aid of the expression:

$$p = \left[ \frac{\text{real sp. gr.}}{\text{apparent sp. gr.}} - 1 \right] 1000$$

An absolutely non-porous rubber will, of course, give $p = 0$. Porosity is not a factor which one meets very often in vulcanised rubber articles, and the apparent and true specific gravity will usually be identical. Where samples are shown to be porous, it is usually the result of faulty manufacture, rather than the use of any particular constituent of the compound. An undue percentage of moisture in the compound, or the undercuring of a stock containing high oil, waste or reclaimed stocks, will be apt to show a considerable degree of porosity ("blowing"), but articles showing such defects are ordinarily easily recognised, classed as defectives, and are not likely to be included in any material which would be subjected to analysis or other tests.

The *tensile strength* and *elongation*[1] of rubber are useful mechanical tests, but necessitate somewhat complex apparatus for their exact determination. The most successful forms of apparatus so far devised appear to be those of Schopper, of Leipzig, and Scott, of Providence, Rhode Island, U. S. A.

**Electrical tests** of insulation resistance, high-voltage tests, and measurements of electrostatic capacity are also valuable in certain cases.[2]

Many samples of rubber are liable, when exposed to light to develop superficial cracks, due to oxidation, this phenomenon being usually referred to as "*sun-cracking*." To measure this tendency, Weber suggests the use of a mixture of 20 grm. of acetone and 60 c.c. of a 20% solution of hydrogen peroxide. The solution is allowed to stand for a fortnight before being used; it will keep for a long time. Weighed strips of equal area of the sample to be tested and of the standard with which it is to be compared are immersed in the solution for at least two days, and are then withdrawn, washed with acetone and water, and dried at 100°. The increase in weight shows the amount of oxygen absorbed. Ditmar (*Anal. d. Kautschuks, etc.*, 1909, 239) heats the rubber sample in oxygen at 100°, and determines the loss or gain in weight incurred thereby.

The dry heat test has been developed to its most practical state by W. C. Geer (*India Rubber World*, 1916, **55**, 127–30; 1921, **64**, 887–92). In this test, the rubber test sheets are exposed to hot, dry air, in the dark, at a temperature of about 70°. Tensile and

[1] On the subject of the "tensile" properties of rubber, see Schidrowitz, *Ind. R. J.*, 1909, **37**, 313, 381, 521; see also *Gummi-Zeit.*, 1909, **23**, 1177–1179; *Ind. R. J.*, 1909, **38**, 41; Tuttle "Analysis of Rubber," 143–8.
[2] *Cf.* C. O. Weber, *Chem. of Ind. R.*, 1902, pp. 230, 234.

elongation tests are made at predetermined intervals, and 24 hours of such treatment are assumed to produce a deterioration such as would be produced by, say, six months of natural ageing. The best and most useful results are obtained when two stocks of the same type are compared.

The principal objection to this method, and it is a very serious one, is that deterioration of rubber is produced by two elements, viz., heat and oxygen. If the heat test proper is desired, then it should obviously be conducted in an atmosphere of inert gas; if the effect of oxygen is to be studied, then the temperature should be reduced to the point where the effect due to the oxygen is many times greater than the effect due to the heat. This, in fact, has been done by Bierer and Davis (*Ind. Eng. Chem.*, 1924, 16, 711–7), who reported to the meeting of the Rubber Division of the American Chemical Society, April 21–26th, 1924, the conclusions which they have reached as a result of the study of thousands of tests made on all sorts of rubber stocks exposed to oxygen under pressure at varying temperatures. They report that the ageing in oxygen is more nearly comparable to natural ageing, than the Geer test.

Tuttle showed that during the course of natural ageing (*India Rubber World*, 1916, 55, 129; 3rd *Annual Report Nat. Advisory Comm. for Aeronautics*, 1917, 463–6) the acetone extract increased with the deterioration of the rubber. In the Geer test, this change in solubility does not occur, whereas Bierer and Davis point out that this is always present in natural aging, and their method for heating in oxygen reproduces this feature of natural ageing as well as the effect of the reduction in the tensile properties. It is to be hoped that our co-operating committees will make a thorough investigation of the Bierer and Davis method, for it does seem to hold forth promise of being a method which will really predict the useful life of an article, and as such should be very welcome to those who purchase rubber articles by specifications.

The inorganic materials mixed with rubber during manufacture are used: 1. as "fillers," that is, merely to reduce the cost of the manufactured article; 2. as sulphur carriers, which hasten the vulcanisation of the rubber or influence it in some way; 3. as pigments, to give the finished article a definite colour; or 4. to heighten in the rubber some desirable physical or mechanical property. It is not possible, however, to draw a hard and fast line between these 4 classes of

ingredients.   Some of the sulphur carriers, for example, are as much used for their "filling" properties and for their colouring value as for any influence they have on vulcanisation.   The compounding materials employed are usually practically insoluble in water, and chemically inert at temperatures ranging from 180° to 200°.

Since red lead is a hardening agent in india-rubber and is used in admixture with the "soft" brands of rubber, the presence of this inorganic material sometimes constitutes evidence in favour of the low quality of the rubber in the sample.   Barium and calcium hydroxides have a remarkable hardening effect upon rubber, and are frequently added in small quantities for this purpose.[1]

The *ash* left on the ignition of rubber articles is not a true criterion of the amount of mineral matter in the original sample.   Neither do the constituents of the ash represent truly those of the original mixing.   This is due to the reducing action of organic matter upon inorganic substances (as, for example, sulphates) and to the fact that part of the organic sulphur reacts with metallic oxides to form sulphides.   Some compounds (such as those of antimony and mercury) volatilise more or less completely on ignition, and carbonates are more or less converted into oxides.

Notwithstanding these sources of error, an estimation of the "ash" is of distinct value, provided the above considerations are borne in mind.   The estimation should be carried out by careful ignition of 1 grm. of the finely divided sample in a thin layer in a porcelain dish, or large crucible, preferably with the outside unglazed; as low a temperature should be employed as possible, and the heat regulated so that the vapours given off do not inflame.   It is only occasionally that the ash represents accurately the mineral content of the compound.   It is distinctly unreliable in any of the calculations of rubber content by difference methods.   It is retained in the repertoire of the rubber chemist solely because of all the methods suggested for the estimation of rubber, it is the least time-consuming,

[1] Heinzerling and Pahl have recorded the results of an extensive research into the influence of various inorganic and organic admixtures in rubber (*J. Soc. Chem. Ind.*, 1892, **11**, 536). Their results show that the quality of rubber is much improved for some purposes by the addition of certain mineral matters.   Rubber vulcanised with 10 % of sulphur was found to be the most elastic.   All mineral and organic substances diminished the elasticity of rubber goods, while the addition of oxides of zinc, lead, magnesium and calcium, calcium carbonate, pitch and glycerin, increased their strength.   Organic admixtures, such as paraffin-wax, rosin and pitch, and small quantities of oil substitutes, increased the insulating-power of rubber, but the mixtures did not resist the action of high temperatures so well as pure rubber.   Certain mineral matters, such as the oxides of zinc, calcium and magnesium (the last-named only in small quantities), and calcium carbonate also increased the insulating power of rubber.   Large quantities of magnesium oxide, however, and additions of vermilion and lead oxide decreased the insulating-power.   Rubber containing certain organic admixtures (such as paraffin-wax, asphalt, and oil substitutes) was found to have an increased power of resisting the destructive action of oil.

and requires the least equipment.   It has been made a part of some of the specifications for the examination of manufactured rubber goods, but to accept or reject a delivery of rubber goods on a specification of a minimum and maximum percentage of rubber, and estimating that percentage by means of an ash determination, is an absurdity bordering on the ridiculous.

The residue obtained on an ignition should never be used for the analysis of the mineral content.   A method for this procedure is given on page 382.

**Dry and Moist Heat Tests.**—Taken together, these two tests are known as the "British Admiralty Test."   They are sometimes useful as showing what effect heating, in contact either with air or with steam, will have upon the sample.

**The dry heat test** (*cf.* Geer, page 377) is carried out by exposing a small sample of the rubber to a temperature of 132° for a stated time, usually 2 hours, in a hot-air oven.   The deterioration brought about is noted by inspection or by the application of physical tests (tensile strength and elongation) before and after heating.

**The moist-heat test** is applied by heating a second sample of the rubber in steam at a temperature of 160° for 4 (or 3) hours; the operation may be conducted either in a sealed glass tube or in an autoclave.   The steam pressure should be released very slowly at the conclusion of the test, in order to avoid breaking up the surface of the rubber, into which the steam penetrates during the test. Contamination of the sample with the copper of the autoclave should be carefully avoided, if the sample is to be examined at an interval after the test is carried out, as such contamination renders the sample liable to rapid deterioration.   Samples containing rubber substitute are, as a rule, very badly deteriorated by the moist-heat test.

For the complete analysis of vulcanised rubber samples, the scheme shown on page 382, adapted from processes devised by Weber, Henriques, and others, may, in general, be followed.

It is rarely necessary, however, to go through the whole scheme with any one sample.   The process may be considerably shortened, for example, in the case of samples, the mineral matter of which contains no sulphur, and the detailed composition of which is not of first importance.   If, in addition, the sample is of the "red" variety, the process may be further curtailed by the omission of the chloro-

form extraction, since these varieties are not likely to contain tar, pitch, or bituminous matters. The method of procedure in such cases is as follows:

| 2 grm. of the sample are extracted with acetone (see below). | | |
|---|---|---|
| **Soluble in Acetone.** | **Residue.** Extracted with alcoholic potassium hydroxide. | |
| (See table on p. 382.) | **Soluble in Alcoholic Potassium Hydroxide**<br><br>Chlorosulphide substitutes.<br>Sulphide substitutes.<br>Oxidised (blown) oils<br>Polymerised oils.<br>Sulphur in substitutes.<br>Chlorine in substitutes. | Residue (rubber, mineral-matter, etc.).<br><br>Sulphur in rubber (= S. of vulcanisation).<br>Chlorine in rubber. |

Any antimony pentasulphide present will go into solution to some extent in the alcoholic potassium hydroxide, from which it must be reprecipitated and its amount estimated.

**The mineral matter** should also be estimated by careful ignition: the india-rubber of the sample is then obtained by difference.[1]

**The sulphur of vulcanisation** can, in this case, be estimated directly on a portion of the above residue from the alcoholic potassium hydroxide treatment by the method used for total sulphur (p. 400), while the *chlorine of vulcanisation* may be determined on the remainder of the residue by one of the methods described on p. 402. Reference must, however, be had to the precautions dealt with on p. 379.

The various methods employed under the above schemes of analysis are carried out as follows:

The apparatus used for the making of the acetone extraction of vulcanised rubber, as well as other types of rubber, and also for making such other extractions as may be desired, should be of the Cottle or similar type, and should conform to the following requirements: it should be of the reflux type, with the condenser placed immediately above the cup which holds the sample; the sample must be suspended in the vapour of the boiling solvent, the cup must be of the siphon type; the cup must be far enough away from the sides of the extraction flask that it will be maintained at the temperature of the boiling point of the solvent; only glass or metal joints may be used, there shall be no cork, rubber, or similar material in the extractor, with which the solvent may come in contact, and from which extractable material may be obtained.

[1] *Cf.* page 379 for statements regarding the value of such estimations.

## SCHEME OF RUBBER ANALYSIS

2 grm. of the sample are extracted with acetone (page 381).

| (A) Soluble in Acetone. | (B) Residue. Extracted with chloroform. | | | | |
|---|---|---|---|---|---|
| Resinous constituents of india-rubber. Fatty oils. Mineral oils. Resin oils. Solid hydrocarbons. Resins. Free sulphur. Part of M. R. | (C) Soluble in Chloroform. | (D) Residue. Extracted with alcoholic potassium hydroxide. | | | |
| | Tar. Pitch. Bituminous substances. Sulphur in above. Part of M. R. | (E) Soluble in Alcoholic Potassium Hydroxide. | (F) Residue. Extracted with solvents.[1] | | |
| | | Chlorosulphide substitutes. Sulphide substitutes. Oxidised (blown) oils. Polymerised oils. Sulphur in substitutes. Chlorine in substitutes. | (G) Soluble. | (H) Residue. Extracted with boiling water. | |
| | | | India-rubber. Sulphur in india-rubber. Chlorine in india-rubber. (The total of the above 3 constituents is determined by loss.) | (I) Soluble in boiling water. | (K) Residue. |
| | | | | Starch. Dextrin. Glue. Albumin. | Mineral matter. Free carbon. Fibrous materials. Sulphur in inorganic compounds. |

[1] The choice of solvents is quite extensive, although few can be relied upon to any considerable extent. Xylene and petroleum oils are worth trying.

Take 2 grm. of the finely divided sample, place in the extraction thimble, and extract for 8 hours. The acetone may be distilled and the residue weighed in the extraction flask, or the acetone extract may be transferred to a smaller tared flask, the acetone distilled and the residue dried at 90 degrees to constant weight.

The general nature of the *acetone extract* will often give sufficient indication of its composition; a complete analysis may frequently be almost impossible. A clean extract, light in colour, is obtained in the case of a sample free from substitutes and similar additions. If the extract is a more or less viscid liquid, solid hydrocarbons and solid resins are probably absent, unless their presence is masked by that of some other liquid constituent. Mineral oil usually imparts to the acetone solution a characteristic fluorescence, and its presence may be confirmed by warming the acetone extract with a small quantity of absolute alcohol, when mineral oil remains undissolved. Resin oils may be detected by the purple coloration obtained with carbon disulphide and stannic bromide or by the similar colour produced by acetic anhydride and sulphuric acid (the Liebermann-Storch test). Mineral or resin oil may not have been added to the mixing as such, but as constituents of "reclaimed" or "recovered" rubber. Tallow may also be present in the extract. If voluminous flakes separate from the warm alcoholic or acetone solution on cooling, solid hydrocarbons (paraffin-wax, ceresin, ozokerite) are present.

Paraffin-wax tends to protect the rubber from oxidation, probably by decreasing its microporosity; it has, however, the effect of decreasing its tensile strength.

**Fatty oils** may be estimated approximately by Koettstorfer's process, according to which the acetone extract is saponified with a known volume of standard alcoholic potassium hydroxide, the excess of alkali being afterward estimated by means of standard acid. The fatty oil may be calculated in terms of colza oil, 1 grm. of which requires for its saponification 0.172 grm. of KOH. It should, however, be remembered that certain resins also are partially saponified by KOH. The resins of *Hevea brasiliensis* are saponifiable to the extent of from 50 to 80%.

It has been stated that a separation of the various constituents of the acetone extract may be effected by means of aqueous and alcoholic solutions of chloral hydrate of definite strength.[1] Experi-

Cf. Weber, *J. Soc. Chem. Ind.*, 1903, 22, 576; Allen, 1907, Vol. 2, Pt. 3, pp. 299, 300; Lunge, *Chem. tech. Unt. Methn.*, 1905, Vol. 3, p. 353.

ence, however, has shown that the method is altogether unreliable as a quantitative one.[1]  A partial separation may be effected by means of absolute alcohol, as indicated in the following table:

SEPARATION OF ACETONE EXTRACT BY MEANS OF ALCOHOL

| Soluble in alcohol | Insoluble in alcohol |
|---|---|
| Free fatty acids. Resins (colophony). Waxes (beeswax; carnauba). Castor and blown oils. | Fatty and mineral oils (except castor and blown oils). Tar oils; solid hydrocarbons (paraffin-wax). |

It is unnecessary to distinguish between castor and blown oils, since they are of equal value in rubber mixtures.  The former is practically insoluble in light petroleum, the latter are readily soluble.

The percentage of paraffin wax, or ceresin (the two cannot be distinguished in a rubber mixing) is best estimated from the unsaponifiable portion of the acetone extract.

Fatty oils, if present, may either have been added as such to the mixing, or may be derived from the fatty substitutes present.  To a slight extent added fatty oils may undergo vulcanisation and become converted into fatty substitutes during the vulcanisation of the rubber.  Fatty oils are used today to a considerable extent in rubber mixings, chiefly on account of the softening effect which they exert.  The use of such oils, as in the case of mineral oils, materially shortens the time required for certain factory processes, and with the modern use of organic accelerators of the vulcanisation process, the use of some oil to prevent pre-vulcanisation during the preparatory steps in rubber manufacture, is practically obligatory.  The principal fatty oils used for this purpose are cottonseed and palm oils.

Recent investigations have shown that mineral oils have a[2] greater depolymerising effect on vulcanised rubber than the fatty oils have.  The latter then may be expected to give better ageing properties, and for this reason are to be preferred.  Unsaponifiable oils are almost completely dissolved out of the rubber by acetone.

[1] Cf. Axelrod, *Gummi-Zeit.*, 1909, 23, 845; Frank and Marckwald, *Gummi-Zeit.*, 1909, 23, 979.
[2] Aultman and North, *Ind. Eng. Chem.*, 1923, 15, 262–4.

Add to the acetone extract 50 c.c. N/1 alcoholic potash, boil under reflux condenser for 2 hours, and evaporate to dryness. Transfer to a separatory funnel with water and ether, extract the unsaponifiable material with successive portions of ether, unite the fractions, wash them with water, evaporate the ethereal solution in a tared flask, dry to constant weight at 95°.

The Joint Rubber Insulation Committee[1] pointed out that such and, in fact, all methods now in use, include the unsaponifiable resins with the unsaponifiable oils.

The solid paraffins may be separated from the liquid hydrocarbons by dissolving the unsaponifiable matter in boiling alcohol, placing the solution in a freezing mixture, and filtering off the solid hydrocarbons which separate. The unsaponifiable resins remain with the liquid hydrocarbons in solution in alcohol. The alcohol is recovered, the residue dissolved in carbon tetrachloride, and transferred to a small separatory funnel. The resins are destroyed with conc. sulphuric acid, the acid removed, and the carbon tetrachloride washed with water until free from acid. It is then transferred to a tared flask, the carbon tetrachloride distilled off, the residue dried at 95°, and weighed.

The difference between the total unsaponifiable and the sum of the liquid and solid paraffin hydrocarbons, will give the amount of the unsaponifiable resins. Since the difference method contains the algebraic sum of the errors of three separate estimations, the accuracy of the calculation of resin hydrocarbons is not very high, especially in the case of *Hevea* resins, in which the total resin content is only 3 to 4% of which probably 75% is saponifiable.

The free sulphur may be estimated in the extract, either by taking advantage of its sparing solubility in alcohol, compared with that of the organic constituents of the extract, or by oxidation to sulphuric acid and estimation of the latter.

**Free Sulphur.**—The simplest and withal the most accurate method is: To the dried extract add 100 c.c. of water and 3 to 5 c.c. of bromine. (If a very high free sulphur is indicated by the character of the extract, the amount of the bromine should be increased). Allow the flask to stand for half an hour to an hour, boil off the bromine, and when the solution is practically colorless, filter through a folded filter into a small beaker; cover the beaker, heat to boiling,

[1] *J. Ind. Eng. Chem.*, 1914, 6, 75–82.

add 10 c.c. of 10% barium chloride, and after standing overnight, determine barium sulphate as usual. Kelly (*J. Ind. Eng. Chem.*, 1920, **12**, 875-8; 1922, **14**, 196–7) has pointed out·that the acetone extract contains sulphur in combination with organic substances, as well as in the free state, and therefore the estimation of the total quantity of the sulphur in the acetone extract is faulty to the extent of that which is in combination. Kelly's method not only estimates the true free sulphur, and consequently the sulphur still available for further vulcanisation, ·but at times may be a very convenient way for treating the acetone extract. The method follows:

Dry the acetone extract at not over 65°, add 50 c.c. of 75% ethyl alcohol saturated with sulphur. Weigh the flask and contents to 0.5 grm., heat for a few minutes to get the organic matter in solution, then cool slowly. Allow the flask to stand three hours, reweigh and add 75% alcohol, *sulphur free*, to replace the loss. Decant the solution, wash two or three times with 75% alcohol saturated with sulphur, and then dry. The sulphur may then be estimated by any satisfactory method.

Hübener (*Chem. Zeit.*, 1909, **33**, 648–649 and 662–663) oxidises the free sulphur in the original sample to sulphuric acid with bromine water, and estimates the sulphuric acid formed. This method will give low results when appreciable quantities of free sulphur are present.

In drawing conclusions from the amount of organic matter in the acetone extract of a sample, it should be remembered that rubbers which have undergone deterioration, owing to atmospheric oxidation, contain increased amounts of acetone-soluble substances.

The chloroform extract is made in exactly the same apparatus as is used in making the acetone extract. The chloroform should be redistilled over alkali.

Extract for four hours the residue from the acetone extraction (it is not necessary to remove the acetone adhering to the sample), using about 60 c.c. of the solvent. If at the end of four hours, the solvent in the siphon cup is still coloured, continue to extract till it is colourless. Filter the extract through fat-free filter paper into a small Erlenmeyer flask, distil off the solvent, and dry the flask and contents to constant weight at 95°.

If the chloroform extraction cannot be started immediately after the acetone extraction has been completed, the sample should be

protected against oxidation by keeping it in a vacuum desiccator in a vacuum of at least 50 mm. of mercury. Vulcanised rubber which has been extracted with acetone oxidises very rapidly in the air, and the resultant products are so soluble in chloroform as to yield hopelessly false results, being as much as five to ten times the true amount.

Reserve the residue from the chloroform extraction for treatment with alcoholic potassium hydroxide.

The chloroform dissolves part of the rubber, particularly the undercured, and the oxidised rubber. Its chief value is that it dissolves part of the mineral rubber, the solution taking on an intense brown or black colour. It is an invaluable qualitative test for the mineral rubbers, the colour being quite distinctive, and not likely to be mistaken for anything else.

The chloroform extract in a well cured and unoxidised sample of soft vulcanised rubber will run from 1 to 3% of the rubber present, with the average nearer the lower figure. It has been suggested as a means of determining whether or not the rubber has been under-cured, but the data available are largely limited to insulation compounds, and are not entirely convincing.

The percentage of chloroform extract bears no definite ratio to the amount of bituminous substances present in a compound. A considerable quantity of the so-called mineral rubbers will be dissolved by the acetone, and this quantity will vary tremendously in the different types of M. R. employed. For the same reason, no estimation need be made of the sulphur in the chloroform extract. It has no real significance, and the figure cannot be used for the calculation of any constituent of the compound.

**Alcoholic Potassium Hydroxide Extraction.**—Dry the residue from the chloroform extraction at 60° until the odour of chloroform is no longer noticeable. Place the rubber in a 200 c.c. Erlenmeyer flask, and cover with 50 c.c. N/1 alcoholic potassium hydroxide. Boil for four hours under reflux condenser. Filter by decantation through a hardened filter paper, wash with two portions of 25 c.c. of hot alcohol, and then thoroughly with hot water. Evaporate the filtrate to dryness, take up in warm water, and when solution has been effected, cool to room temperature. Transfer to a separatory funnel, add 30 c.c. N/5 hydrochloric acid and sufficient water to bring the total volume up to about 100 c.c. Add 40 c.c. of ethyl

ether, shake thoroughly, allow the liquid to stand until the two layers are completely separated, draw off the water into a second separatory funnel, and continue to extract with 20 c.c. portions of ether until a colourless solution results, and then twice more. Unite all the ether fractions in the first separatory funnel, and wash with water until the water shows no further acidity (test with silver nitrate solution). Filter the ether through a plug of extracted cotton into a weighed beaker or flask, evaporate to dryness, and dry to constant weight at 95°.

In order to ascertain the nature of the substitutes present in manufactured rubber, the *chlorine and sulphur in the alcoholic sodium hydroxide extract* must be estimated.[1] These values are also required to obtain a knowledge of the extent of vulcanisation of the sample. For these estimations, the alkaline alcoholic liquid, with the washings, is evaporated to about 50 c.c., and then made up to a volume of 100 c.c. The chlorine is estimated by evaporating 50 c.c. of this liquid to dryness, and igniting the residue, adding sodium nitrate to assist in the oxidation of the carbon. The residue is dissolved in water, the solution acidified with nitric acid, and any chlorine present precipitated with silver nitrate and weighed in the usual manner. The sulphur is estimated in the remaining 50 c.c. of the original solution, by first of all heating it with bromine on the water-bath, in order to oxidise the alkaline sulphides present, and then evaporating the liquid to a syrup, oxidising with fuming nitric acid, evaporating to dryness and igniting as before. The residue is dissolved in water, the solution filtered, and the sulphate precipitated with barium chloride.

The following deductions from the results of the above methods of analysis have been made by R. Henriques.[2] The presence of chlorine and sulphur in approximately molecular proportions (*i. e.*, about equal weights) in the alcoholic potassium hydroxide extract, indicates the presence of white substitute (chlorosulphide) or a mixture of this with blown-oil substitute. If the sulphur is considerably in excess of the chlorine then both white and brown substitutes are present in the extract, with possibly also blown-oil substitute.[3]

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[1] According to C. O. Weber, when white substitute (chlorosulphide) is used in hot vulcanised rubber goods, as is sometimes the case, it loses more or less of its chlorine in the form of HCl, the whole of which is retained by the rubber sample, a portion of the chlorine combining with the rubber hydrocarbon to form a hydrochloride, whilst in the presence of litharge, calcium carbonate, etc., the remainder is taken up by the mineral matter. The dechlorination of the substitute is, however, far from complete, and the presence of chlorine in the substitute cannot escape detection.

[2] *Chem. Zeit.*, 1893, 17, 707.

[3] But see footnote 1, p. 411.

When sulphur only is present, and no chlorine, the substitute employed is the brown variety, or a mixture of this with blown-oil substitute. If the extract is due to the "brown" substitute alone, it will contain about 10% of sulphur, whereas, at most, only traces of this element will be present in a blown-oil extract. The absence of both sulphur and chlorine in the extract indicates, in the presence of a substitute, that one prepared from blown or polymerised oil has been added. It is impossible to distinguish between fatty oils which have been added to the mixing, and have become vulcanised simultaneously with the rubber and so converted into fatty substitutes, and substitutes which have actually been added as such. Heil and Esch state, however,[1] that practically no vulcanisation of fatty oil occurs at ordinary vulcanisation temperatures, as shown by acetone extraction tests.

The *residue from the alcoholic potassium hydroxide extraction* may be treated with some solvent to separate the india-rubber from the mineral matter. Henriques proposed to dissolve out the former by heating with boiling petroleum, fractions boiling between 140° and 250° F. being used for the purpose.[2]

Axelrod (*Gummi-Zeit.*, 1907, **21**, 1229–1231) finds that by the use of a petroleum distillate boiling at about 300° a complete resolution of vulcanised rubber is effected, and he has applied this observation in the estimation of the pure rubber in rubber goods as tetrabromide. Even with this, however, it is doubtful whether complete solution can be achieved in the presence of rubber with a high coefficient of vulcanisation, such as is found in some samples containing reclaimed rubber, for example. It is important to obtain a method by which the rubber can be conveniently dissolved and separated from the mineral matter, since the incineration of the sample causes loss of various volatile constituents (mercury and antimony compounds), carbon dioxide is driven off from carbonates, carbon pigments, carbohydrates and fibre are burnt, and so on. Weber has therefore suggested the use

[1] *Manufacture of Rubber Goods.* Griffin, 1909, p. 117.
[2] The method of extraction of the sample with boiling petroleum was suggested by Henriques for the separation and estimation of the free sulphur and sulphur of vulcanisation, and that present in the mineral constituents (*J. Soc. Chem. Ind.*, 1893, **12**, 467). The method is, tedious, however, and in many cases—as, for instance, when much mineral matter is present—the solution of the rubber is incomplete. Henriques therefore abandoned the use of this solvent (*Chem. Zeit.*, 1894, **18**, 411, 412 and 422–444), and found it preferable to decompose the sulphides in the finely rasped sample with acid, and to determine the sulphur of the sulphides, and that of the sulphates as described on p. 400. The residue contains sulphur in the form of sulphur of vulcanisation and insoluble sulphates (of lead and barium) which latter can be allowed for by calculation from the bases.

of α-nitronaphthalene, which quickly decomposes and dissolves the rubber of samples heavily vulcanised, and gives solutions which, when diluted with benzene and allowed to stand for a few hours, filter readily and give clear filtrates.

Another disadvantage of the nitrobenzene treatment, which also applies to the nitronaphthalene method and, in general, to all solution methods for estimating the percentage of rubber, is the carbonisation of the rubber matter at the high temperature employed. In the case of nitrobenzene, the difficulty can be partly avoided by the addition of a small quantity (5%) of chloroform, which reduces the temperature from 208° to about 173°.[1]    In the case of nitronaphthalene, however, only an insignificant lowering of the b. p. takes place by the addition of chloroform, and Weber prefers to use a specially made air-bath,[2] standing on a tripod, and having a thin layer of fluffy asbestos fibre inside on the bottom. The weighed residue of rubber and mineral matter (from the alcoholic potassium hydroxide treatment), together with about 60 grm. of α-nitronaphthalene, are placed in a weighed wide-necked flask, which is suspended from the lid of the bath in such a way that it does not come into contact with the sides or the bottom of the bath. The temperature is kept at 180°.    A higher temperature may cause carbonisation of the rubber.    The solution of the rubber is usually complete in an hour, and sometimes a much less time suffices. During the heating the contents of the flask should be frequently stirred gently with a glass rod.    When solution is complete the flask and its contents are allowed to cool, about 150 c.c. of benzene are added, and the liquid is left to stand until the mineral matter settles out.    The solution is then filtered, the residue on the filter being finally washed with benzene, dried at 110° for 1 hour, and weighed.

The loss of weight by the nitronaphthalene treatment represents the india-rubber of the sample, including the sulphur and chlorine of vulcanisation.    The nitronaphthalene solution of the india-rubber does not, however, contain rubber as such, since this has undergone

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[1] C. O. Weber obtained, by the nitrobenzene treatment of 2 samples of manufactured rubber, a considerable amount of carbonaceous matter left with the mineral matter after the rubber had been dissolved.    The mineral matter contained lead oxide, PbO.    When the samples were examined by the nitrobenzene-chloroform method, however, no carbon was obtained, and the mineral matter contained lead peroxide, $PbO_2$, added to the samples as red lead.    At the b. p. of nitrobenzene, lead peroxide undoubtedly oxidises the india-rubber, with production of carbon and lead oxide, PbO.

[2] Obtainable from Messrs. F. Jackson & Co., 11 Half Moon Street, Manchester.

decomposition by the treatment,[1] and cannot be recovered from the nitronaphthalene.[2] For this reason the sulphur and chlorine of vulcanisation cannot be directly estimated in this solution.

Frank and Marckwald have worked out a method for the separation of the mineral matters from a sample of vulcanised rubber, which is free from certain of the disadvantages attending the nitronaphthalene process, but which has itself the slight drawback of necessitating the use of somewhat special apparatus. The process is carried out as follows: (*Gummi-Zeit.*, 1908, **22**, 1344–1346) 1 grm. of the acetone-extracted sample is placed in a stoppered glass vessel, similar in form to an ordinary weighing-bottle, and covered with 30 c.c. of xylene; the vessel is then placed on a suitable support in an autoclave containing xylene; heat is applied in such a way that the pressure rises to 15 atmospheres in about 1 hour, and the pressure is maintained at from 15 to 18 atmospheres during from 3 to 4 hours. The whole apparatus is then allowed to cool, and the vessel containing the sample is removed. If the liquid is clear, and the mineral matter has settled at the bottom of the vessel, it is at once diluted with an equal volume of ether and well stirred. If, however, the liquid be turbid, from 1 to 3 c.c. of alcohol are added to aid clarification, and the liquid is then diluted with ether and allowed to stand overnight. The residue, consisting of mineral matter, carbon, and other added ingredients, is collected on a weighed filter, washed with ether, dried, and weighed. Pontio (*Le Caout. et la Gutta-percha*, 1909, **6**, 2752–2753) recommends the use of cumene at ordinary pressures, for a similar purpose, while Hinrichsen (*Chem. Zeit.*, 1909, **33**, 735–736, 756–757) employs petroleum of high b. p., subsequently diluting the solution with benzol before filtration. Frank and Marckwald (*Gummi-Zeit.*, 1909, **23**, 1522–1524) have criticised this method, and have suggested modifications which, when certain precautions are taken, are said to render the process a passable substitute for the xylene method when an autoclave is not available. 1 grm. of the finely divided (acetone-extracted) sample is heated in a weighed 100 c.c. flask with 25 c.c. of boiling petroleum (b. p. 230° to 260°), or of paraffin oil

[1] The decomposition product is stated by Weber to be similar to caoutchouc, in that it forms an additive compound with bromine, $C_{10}H_{16}Br_4$, which is quantitatively precipitated by alcohol.

[2] The presence of gutta-percha or balata in vulcanised rubber cannot, therefore, be detected by this method of analysis. In rubber articles only slightly vulcanised, gutta-percha and balata can be extracted, according to Weber, by repeated treatment of the original sample with cold benzene, and precipitation of the benzene extract with absolute alcohol. These substances are not, as a rule, present in very large proportions.

(sp. gr. 0.86) until the rubber is completely dissolved.    This occupies from 15 minutes to 1 hour, according to the nature of the sample. The solution is allowed to cool, made up to 100 c.c. with petroleum spirit, light benzine, or ether (benzene should not be used), allowed to stand until clear (from 2 to 10 hours), and filtered through a weighed filter.    The mineral matter on the filter and any remaining in the flask are well washed with the solvent used for dilution, and the filter and flask are then dried and weighed.    The total increase in weight of flask and filter represents the amount of mineral matter in the sample, together with any free carbon or undissolved organic matter.    The mineral matter is now digested with ammonium sulphide, to remove antimony compounds if present, and then with warm, dilute hydrochloric acid to remove all soluble minerals. The residue of insoluble mineral matter and organic matter may now, after weighing, be ignited, and weighed again, any difference in weight being taken as free carbon and organic matter.    During the heating with petroleum or paraffin, magnesium carbonate is partly decomposed, carbon dioxide and water being split off, while antimony pentasulphide loses some of its sulphur and is converted into trisulphide.    Account must be taken of these facts in the analysis of samples containing either of these two substances. It is, moreover, by no means a certainty that the whole of the rubber present will pass into solution even after 1 hour's heating; if not, some will of course be found when the insoluble residue is ignited.

The Joint Rubber Insulation Committee[1] has devised a method intended for insulation compounds containing only new rubber and mineral fillers; for stocks of this type, it is quite reliable.    Mineral rubber, glue, lampblack cellulose, etc., give high results for rubber. The method is:

Add to the rubber residue[2] from the alcoholic potash extraction, sufficient water to make the total volume 125 c.c., and then add 25 c.c. of conc. hydrochloric acid.    Heat for one hour, decant through a Büchner funnel, using hardened paper, and wash with 25 c.c. of hot water; repeat this process twice.    The rubber should

[1] *Am. Inst. Elec. Eng.*, April, 1917.    It is to be noted that the J. R. I. C. procedure was developed solely for use in testing high grade insulation compounds containing 30–40 % of Hevea rubber, paraffin or ceresin, and inorganic fillers only.    Reclaimed rubber, carbon flack, organic oils and softeners (excepting those stated) and organic fillers and wastes, were all prohibited by specification.    Analysts should bear these facts in mind when attempting to apply this method to the analysis of other types of compounds.

[2] In the original J. R. I. C. method of analysis, the size of the sample used is 4.0 grm. If any other amount be employed, a corresponding change in the formula for calculating rubber hydrocarbons should be made.

be white, and free from black specks from undissolved filler (lead sulphide).   Wash the rubber free from chlorides, transfer the rubber to the filter paper, dry as much as possible by suction, wash with 50 c.c. of 96% alcohol, and transfer the entire residue to a weighing bottle.   Dry to constant weight at 95 to 100°.   Let this weight be represented by C.

On a portion of this residue C, estimate the ash E, and the sulphur F in ash E.   Estimate the sulphur H in another portion G of residue C.

To estimate E, place about 0.50 grm. of residue C into a weighed porcelain crucible, heat gradually until the contents of the crucible have ceased smoking, then raise the temperature until all organic matter is destroyed.   Cool and weigh, calling the residue E.   If this residue E is small, the estimation of the sulphur in the ash may be omitted, and F assumed to be zero.   From the data thus obtained the percentage of rubber hydrocarbons in the original material is calculated as follows:

$$\frac{100\,C}{4}\left[1 - \frac{E-F}{D} - \frac{H}{G}\right] = \%\ \text{rubber hydrocarbons}$$

The principal objection to all of these indirect or difference methods is that one can never be sure that there are no organic or inorganic fillers passing into solution, or that insoluble organic compounds are not resulting from the interaction of the rubber and the solvent.   At times, an almost endless number of corrections must be applied, and the results are seldom worth the effort spent on obtaining them.

It is impossible at present to ascertain the proportion of "recovered rubber" in rubber goods, and very difficult to detect its presence. Although in commerce recovered rubber is known as "devulcanised rubber," it not only contains the whole of the sulphur of vulcanisation of the waste rubber from which it was obtained,[1] but also undergoes further vulcanisation in the process of recovery, and therefore a sample containing any quantity of this material will frequently have a higher coefficient of vulcanisation than prior to the devulcanisation.   This "coefficient" is the percentage ratio

[1] R. Henriques (*Chem. Zeit.*, 17, 1266), however, states that in the regeneration of rubber, actual devulcanisation seems to take place by oxidation.   That such is the case is, according to Henriques, shown by the fact that regenerated rubber possesses the plastic properties of natural raw rubber to some extent, and also on analysis of a "recovered" sample, a large quantity of sulphates was found to be present, and but little sulphur in organic combination.   An examination by Henriques of further samples containing only about 50 % of real rubber showed, however, a proportion of sulphur of vulcanisation ranging from 0.71 to 2.03 %.

between the amounts of india-rubber and sulphur of vulcanisation of the sample. Thus, if a sample has been found to contain 50% of real rubber substance and 2% of vulcanisation sulphur, its "coefficient of vulcanisation" will be 4%. The coefficient of vulcanisation was formerly believed to be useful in estimating the percentage of reclaimed rubber, but with present day methods of manufacture, this is not possible. The coefficient obtained when curing with organic, is much lower than when curing with the inorganic accelerators, and whereas the latter usually have a coefficient between 3.5 and 4.0, there are some organic accelerators which give a very satisfactory product at a coefficient around 1.5/2.0. The coefficient of vulcanisation is consequently not only of no use in estimating the approximate percentage of reclaimed rubber, but is of little value in indicating the optimum or best cure.

The composition and properties of recovered rubber are described on page 413.

**Direct Estimation of Rubber in Vulcanised Rubber Samples.—** The main point of weakness in the scheme of analysis described above is that the essentially important constituent, the rubber itself, is estimated by difference. During recent years a number of methods have been devised having for their object the direct estimation of the rubber in a sample of vulcanised rubber. The method proposed by Axelrod (*Gummi-Zeit.*, 1907, **21**, 1229–1231; *cf.* Budde, *Gummi-Zeit.*, 1907, **21**, 1205–1208) has been found to be of value in a number of instances, although, as at present carried out, its application would appear to be limited. In common with other similar processes, based on the formation of bromine addition compounds of rubber, Axelrod's process has been subjected to criticism by Harries and Rimpel (*Gummi-Zeit.*, 1909, **23**, 1370–1371), who find that whereas the whole of the rubber is assumed to be converted into an insoluble bromine derivative, there is, in fact, a portion of it which remains in solution in the liquids employed.

Since then, the tetrabromide method has been a subject of almost endless controversy. Probably the best procedure today is that of Fisher, Gray and Merling (*J. Ind. Eng. Chem.*, 1921, **13**, 1031–4). Extract a 2.0 grm. sample of crude rubber with acetone. Dry the residue in an inert atmosphere, dissolve in carbon tetrachloride, and make up to 500 c.c. To 50 c.c. of this solution, add 30 c.c. 0.5/N bromine, leave for $2\frac{1}{2}$ to $3\frac{1}{2}$ hours in a darkened

room or closet. Add 15 c.c. of 20% KI, and titrate with 0.25/N thiosulphate.

To estimate the substitution bromine, add 10 c.c. of 5% potassium iodate, titrate the liberated iodine, and calculate the equivalent bromine. The difference between the total bromine lost during bromination, less twice the amount estimated as substitution bromine, is the bromine addition value.

For vulcanised rubber, use tetrachlorethane in place of the carbon tetrachloride. If oil substitutes, or factice, are present, make an alcoholic potassium hydroxide extraction in addition to the acetone extraction. After the alcoholic potassium hydroxide extraction, remove the alcohol, add lime, and prolong the heating to about 12 hours. An aliquot portion of this is taken and treated as under crude rubber.

The sulphur of vulcanisation is estimated, and this is used in calculating the total rubber content, assuming that each atom of sulphur is equivalent to two of bromine.

Thus it will be seen that by this latest procedure, three separate estimations must be made in order to calculate the percentage of rubber. The accuracy of the results is not as good as could be desired. It is probable that by more rigid definition of the procedure, a higher degree of accuracy could be obtained, but until this is done, we must expect to encounter some sizable errors in this analysis. Besides the ordinary errors, caused by manipulation, other disturbing factors may be encountered, such as organic substances containing double bonds, or organic substances containing sulphur which may interfere with the accuracy of the estimation of the coefficient of vulcanisation.

A more accurate method, although curiously enough not so well known and recognised as it should be, is a development of the nitrosite method first proposed by Harries (*Ber.*, 1901, **34**, 2991–2; 1902, **35**, 3256; 4429; 1903, **36**, 1937). Lack of uniformity in the products obtained introduced errors of such size in the Harries procedures as to prevent their use for the estimation of rubber. However, Wesson (*J. Ind. Eng. Chem.*, 1913, **5**, 398; 1914, **6**, 459–62; 1917, **9**, 139–40) saw that throughout these various procedures, one element, the carbon, went through unchanged, and he conceived the idea of estimating the carbon in the nitrosite, and from this figure calculating the original rubber substance. Tuttle and Yurow (*India Rubber*

*World*, 1917, **57,** 17–8; *Bureau of Standards Tech. Paper* 145, 1919) revised Wesson's method, and found that the revised method gave results for rubber with considerable accuracy, even with a very wide range of fillers, both organic and inorganic.   The procedure which they recommend is as follows:

Take o.500 grm. of finely ground rubber (call this weight W), and extract with acetone, chloroform, and alcoholic potassium hydroxide. Dry the residue in hydrogen, or some other inert gas, for 2 hours at 100°. Place the sample in 50–75 c.c. of chloroform, and allow it to swell. Pass into this, until the green colour which is formed persists for 30 minutes, the gases formed by heating arsenic trioxide and nitric acid of sp. gr. 1.30.   To avoid contamination, it is important that no rubber connections be used.   Immerse the flask containing the rubber in cold water during the nitration.   Allow the solution to stand overnight; the next day, filter off the nitrosite through a Gooch crucible, and wash with small quantities of chloroform.   Remove the acid gases and chloroform from the flask by means of a gentle current of air.   Evaporate the filtrate to dryness.   Dissolve the nitrosite remaining in the flask, in the Gooch crucible, and in the residue from the filtrate, in acetone, and filter the solution through asbestos into a weight burette.[1]   The total volume should be about 100 c.c.   Allow this solution to stand for a short time to allow any sediment to settle out in the bottom of the weight burette.   Weigh the burette before and after filling, calling the difference N.   Draw off about 25 c.c. into a small Erlenmeyer flask, reweigh the burette, and call the difference O.   Evaporate the portion drawn off to a small volume, transfer to a porcelain boat (about 14 cm. long and 1 cm. wide), which has been filled with alundum, and wash the flask with acetone (it is best to make this transfer in small portions, drying the boat and contents for a few minutes between each addition).   After the final washing and drying, add 1 to 2 c.c. of a 1% solution of ammonia in distilled water, and dry in  an inert gas for one hour at 90°.   Repeat with a second portion of ammonia and dry as before. By this means, all of the organic solvent is removed.

Place the boat in a combustion furnace,[2] and proceed with the combustion.   Pass the products of the combustion through U-tubes or other satisfactory absorption tubes, placed in the following order: (*a*) (*b*) (*c*), potassium dichromate—conc. sulphuric acid; (*d*), 20 mesh

[1] For the special form of weight burette recommended, see the sketch in Bureau of Standards Tech. Paper No. 145.
[2] Wesson devised a very useful type of combustion apparatus for this work.

powdered zinc; (e) (f), soda-lime and calcium chloride; (g) potassium dichromate and conc. sulphuric acid; (h) dilute palladium chloride solution.[1] Weigh (e) (f) and (g) before and after each combustion; refill (c) and (g) frequently from the same stock solution, so that the gases which enter (e) and those which leave (g) will have the same moisture content.

The carbon dioxide will equal the algebraic sum of the differences in tubes (e) (f) and (g). Call this sum P. The factor for calculating from carbon dioxide to rubber hydrocarbons, is o.309. The formula is therefore as follows:

$$\frac{P \times 0.309 \times N \times 100}{O \times W} = \% \text{ of rubber hydrocarbons.}$$

Correct this figure for whatever extractions were made previous to nitration.

In case the extractions contain material other than rubber, the corrections applied must be arbitrary. It will be recalled that the true resin content of high grade rubbers is about 4%, and the normal chloroform and alcoholic potassium hydroxide extracts of well vulcanised soft rubbers are about 2% and 1% respectively.

**The residue from the nitronaphthalene treatment** (or from the treatment with xylene, paraffin, etc.), may contain carbohydrates, fibrous materials, mineral matters, and the sulphur of the mineral constituents. The residue on the filter is therefore washed with boiling water (about 200 c.c.) in small quantities at a time, which will remove all dextrin or soluble starch; these may be detected in the filtrate by means of iodine. The previous treatment with nitrobenzene or nitronaphthalene will have converted any starchy matter into soluble starch or (chiefly) dextrin. If either of these substances, which are simply filling materials, be found, the loss in weight, after drying the residue, should be noted. In order to ascertain whether dextrin or starchy matter was originally added to the rubber, a little of the sample is boiled with water for a few minutes and one or two drops of a solution of iodine are added to the cooled liquid. Dextrin is only very rarely employed. It should be remembered that certain mineral constituents may be soluble in water (calcium sulphate, etc.).

[1] Very little palladium chloride is needed; use about a drop of a 10% solution in 10 c.c. of water. Its purpose is to detect carbon monoxide, which would indicate incomplete combustion, and a loss of carbon. Carbon monoxide reduces palladium chloride to metallic palladium, which appears as a dense black precipitate. It is very sensitive, and any blackening of this solution shows a loss of carbon; if this should occur, discard the results of the analysis, and start with a fresh portion of the acetone solution of the nitrosite.

**The residue from the treatment with boiling water** should be carefully examined under the microscope for animal or vegetable fibres. These, when present, can be separated from the mineral matter, if their estimation be of sufficient importance, by shaking up a known weight of the residue with chloroform. Weber recommends that the operation be carried out in a test-tube, the residue being gently shaken with about 20 c.c. of chloroform, and the liquid then allowed to stand. The tube is occasionally tapped to assist the separation, and when the mineral matter has settled and the fibres have risen to the top, a pipette containing chloroform is dipped under the surface of the chloroform in the tube, which is then held in an inclined position, and the chloroform in the pipette allowed to flow out. The chloroform in the tube will overflow, carrying the fibres with it, and these should be received in a dish, the chloroform being subsequently evaporated and the residue of fibres weighed. The amount of fibre in the whole residue is then calculated.

The presence of carbon (lamp-black, etc.) in the residue from the water extraction will be recognised by its appearance.

Smith and Epstein (*J. Ind. Eng. Chem.*, 1914, **6,** 75–82) estimate free carbon as follows: Extract 0.500 grm. of rubber for eight hours with a mixture by volume of 68% chloroform and 32% acetone. Transfer the sample to a 250 c.c. beaker, and heat until it no longer smells of chloroform. Add a few c.c. of hot conc. nitric acid, and allow the beaker to stand in the cold for 10 minutes. Add 50 c.c. more of hot conc. nitric acid, taking care to wash down the sides of the beaker; heat on the steam bath for at least an hour. While hot, decant the liquid through a Gooch crucible containing a thick pad of asbestos, taking care to keep the insoluble matter completely in the beaker. Wash with hot nitric acid and suck dry. *Empty the filter flask.* Wash the insoluble residue with acetone, and then with a mixture of equal parts of acetone and chloroform, until the filtrate is colorless. The insoluble matter, which has been carefully retained in the beaker, is digested on the steam bath for 30 minutes with 35 c.c. of a 25% solution of sodium hydroxide. Dilute to 60 c.c. with hot water, filter the solution, and wash with a hot 15% solution of sodium hydroxide. Test for the presence of lead by running some warm ammonium acetate solution containing an excess of the hydroxide through the pad into sodium chromate; if a yellow precipitate is obtained, the pad must be washed until the washings no longer give

a precipitate with the sodium chromate solution. Next wash the residue a few times with hot conc. hydrochloric acid, and finally with warm 5% hydrochloric acid. Remove the crucible from the funnel, taking care that the outside is perfectly clean, and dry in an air bath at 150° to constant weight. Burn off the carbon at a dull red heat, cool and reweigh; the difference in weight is approximately 105% of the carbon originally present in the compound in the form of lampblack or gas black.

The estimation of the various mineral constituents of the residue is carried out in the usual way.[1] The most usual inorganic substances employed are: Litharge; Paris white, whiting, zinc white (oxide); lime; barium sulphate; lithopone, which is a mixture of zinc sulphide and barium sulphate; "golden sulphide" of antimony; magnesia; red lead; ferric oxide, and French chalk (whiting). In addition to these china clay, vermilion, plaster of Paris, gypsum or pearl white, white lead, kieselguhr and other siliceous earths, zinc sulphide, lead sulphide, thiosulphate and sulphate, graphite, magnesium carbonate, pumice-stone powder, mica, zinc dust, aluminium powder, iron and brass filings, and asbestos are also used. The microscopical examination of the mineral matter will frequently give much useful information as to its composition.

The total sulphur in the mineral matter is estimated by the same method as used for the total sulphur in the compound (see below).

[1] To prepare a solution for the estimation of the mineral constituents of a rubber compound: Dissolve 2.5 grm. of finely ground rubber in fuming nitric acid; remove the silica by repeated evaporations with hydrochloric acid, and filter. Reserve the insoluble portions. Heat the filtrate and add barium chloride in slight excess. Filter off the barium sulphate (which may be discarded), and transfer the filtrate to a graduated flask. The insoluble residues are fused with sodium carbonate in a nickel dish, the cooled melt dissolved in water, and filtered. The filtrate is examined for silica. The insoluble carbonates are dissolved in dilute hydrochloric acid, and added to the other portion of fillers in the graduated flask, the contents of which are made up to the mark. A 250 c.c. flask is very satisfactory size for the purpose, and 50 c.c. of this solution contains the fillers from 0.500 grm. of rubber.

This procedure introduces two elements: nickel, which is seldom, if ever, found in a rubber compound, and barium, the estimation of which is usually made on a separate sample. The method for this is as follows: To the ash of 1.000 grm. of rubber, add a drop or two of concentrated nitric acid, and heat to dryness, add sodium carbonate, and heat to a gentle fusion. Extract with water, dissolve the insoluble carbonates in dilute hydrochloric acid, nearly neutralise the excess of acid, and remove the lead wth hydrogen sulphide. The barium is precipitated from the filtrate from the lead sulphide in the usual way.

The presence of copper in rubber goods is very undesirable, owing to its deleterious influence on the rubber, especially in the case of cold vulcanised (sulphur chloride) goods. In such cases the copper, even when present in very small quantity, is converted into cupric chloride, which dissolves in the resinous and oily substances present in rubber goods, and therefore permeates the whole material, and gradually hardens and destroys the rubber. (See also Bing, Zeit. f. Chem. u. Ind. d. Kolloide, 1909, 4, 232–235.)

For the detection of small quantities of copper in rubber goods, C. O. Weber ignites 2 or 3 grm. of the sample in a porcelain crucible till all carbonaceous matter is destroyed. The ash is moistened with a few drops of nitric acid, dried, and heated to redness for a few minutes. It is then treated with a slight excess of dilute sulphuric acid, the solution filtered and the residue washed with a small quantity of boiling water. The filtrate is neutralised (or left very faintly acid) by the addition of sodium hydroxide, and tested with zinc sulphide paper. The method is stated to be more sensitive than the ferrocyanide test, allowing of the detection of 0.007 % of copper.

**Sulphides.**—Stevens (*Analyst*, 1915, **40**, 275–81) estimates the sulphide sulphur as follows: The apparatus consists of a Kipp generator for carbon dioxide, a 250 c.c. flask with an inlet tube reaching nearly to the bottom of the flask, and a ground-in stopper carrying an outlet tube (an all glass wash bottle can readily be adapted for the purpose), and connected with the outlet tube are two absorption tubes containing lead acetate solution. Place in the flask 10 c.c. of conc. hydrochloric acid, and 20 to 30 c.c. of ether, pass a current of carbon dioxide through the apparatus until all the air is removed; then remove the stopper, and add the sample of rubber (approx. 1.0 grm.). Again pass carbon dioxide through the apparatus for about 30 minutes, with occasional shaking of the flask. During this period, the acid decomposes the sulphides, liberating hydrogen sulphide, which is absorbed in the lead acetate solution. Heat gently to drive off the last traces of hydrogen sulphide.

The lead sulphide may be estimated in any desired way. If pure nitrogen is available for sweeping out the apparatus the simplest procedure is to use sodium hydroxide to absorb the hydrogen sulphide, and precipitate the sulphur with barium chloride after oxidising with bromine water.

**Sulphates.**—Ignite a 1.00 grm. sample in a porcelain boat, in an atmosphere of carbon dioxide. Boil the residue with sodium carbonate and filter. Acidify the filtrate with hydrochloric acid, and boil to expel sulphur dioxide (from sulphites). Precipitate the sulphates with barium chloride as usual.

If the alkaline filtrate from the above were treated with bromine water, the sulphites would be oxidised to sulphates, and one could therefore estimate the sum of the two. The sulphates alone would be estimated on another sample, and the amount of the sulphates subtracted from the total sulphates and sulphites would give, by difference, the sulphites alone.

Or, if desired, the sulphur dioxide driven off during the estimation of the sulphates could be absorbed in a basic solution, oxidised to sulphates, and a direct estimation made of the quantity.

**Estimation of Total Sulphur** (Waters and Tuttle, *J. Ind. Eng. Chem.*, 1911, **3**, 734–7). Place 0.500 grm. of rubber in a porcelain crucible of about 40–50 c.c. capacity, add 20 c.c. of conc. nitric acid

saturated with bromine, cover the crucible with a watch glass, and allow it to stand for 1 hour. Heat the crucible gently for 1 hour, then remove the watch glass, rinsing it with a little water, add 0.1–0.2 grm. potassium nitrate, and evapoate to dryness. Add 5 grm. of a mixture of equal parts of potassium nitrate and sodium carbonate, and 1–2 c.c. of distilled water, digest for a few minutes, spread the paste along the sides of the crucible, and dry on a steam bath. Fuse the mixture, being careful to avoid contamination with sulphur from the flame. When the fusion is cold, place the crucible and contents in a beaker with about 250 c.c. of water, and heat for several hours; filter off the insoluble carbonates, washing with hot water. The total volume of the filtrate should be between 300 and 400 c.c. Add 7 to 8 c.c. conc. hydrochloric acid, cover the beaker, and allow to stand overnight, filter off the precipitated barium sulphate, ignite carefully over a low Bunsen flame, cool and weigh. Calculate to sulphur, using the factor 0.1373.

**The sulphur of vulcanisation** may now be calculated, from the results of the various sulphur estimations, by subtracting the sum of the sulphur found in various forms from the total sulphur of the sample.[1] Owing to the importance of this figure, however, it is desirable to obtain a more direct estimation. This may be done by reproducing the residue F (page 382) by means of the necessary extractions on about 1 grm. of the sample, estimating the total sulphur in the residue by the process used for the estimation of total sulphur, and subtracting from the result obtained the amount of sulphur found in the mineral matter, which gives the sulphur in the rubber.[2]

The sulphur of vulcanisation may also be estimated directly from the nitrosite (cf. page 396). An aliquot portion of the acetone solution of the nitrosite is weighed from the weight burette into a porcelain crucible, the acetone removed, and the sulphur in the residue estimated by the method of Waters and Tuttle. This is probably the most accurate of all the methods suggested for the estimation of the coefficient of vulcanisation, and deserves wider recognition.

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[1] In the case of rubbers free from mineral matter, or of rubbers the mineral matter of which is free from sulphur, a direct estimation of the sulphur of vulcanisation can be made. See also Budde, *Gummi-Zeit.*, 1909, 23, 1143–1144.
[2] See also Buddé, *Gummi-Zeit.*, 1909, 23, 1143–1144; Hübener, *Chem-Zeit.*, 1909, 33, 144–145 and 155–157.

**The chlorine** in a sample of rubber may be estimated by Carius' well-known sealed-tube method, using about 0.3 grm. of the sample[1] together with 5 c.c. of fuming nitric acid and 1 grm. of silver nitrate. Most rubbers contain mineral matter insoluble in nitric acid, and when this is the case, the mixture of silver chloride and insoluble mineral matter may be treated with dilute sulphuric acid and metallic zinc in a platinum vessel, the liquid being frequently stirred. When the decomposition of the silver chloride is complete, the liquid is filtered or decanted from the insoluble matter, and the chloride precipitated, or titrated with silver nitrate.

A more convenient process for the estimation of chlorine consists in oxidising the rubber by very careful fusion in platinum[2] with a mixture of two parts of sodium carbonate and one part of potassium nitrate. The product is dissolved in water, and the chloride in the filtered liquid estimated as silver chloride.[3]

A general examination of the original rubber will frequently give valuable information as to the composition of the mineral matter present, and the form in which it occurs. Generally speaking, "grey" rubber contains no colouring-matter. Red rubbers may contain antimony pentasulphide, mercuric sulphide, or ferric oxide,[4] or, in some instances, in the case of cold-vulcanised articles, red "lake" pigment. Black rubbers are either desulphurised grey, or "cut-sheet," or they contain lamp-black, pitches, or similar compounds. Water may dissolve out certain constituents, such as calcium sulphate, from the finely rasped sample. Weber found 6% of sodium carbonate in a sample of rubber, but this is most unusual in anything but sponge rubbers. Hydrochloric acid may separate other substances. The presence of lead sulphate in rubber may be detected and its amount estimated by boiling a known weight of the finely divided (rasped) sample with ammonium acetate solution for about half an hour, and precipitating the lead from the solution after filtration (*Cf.* Schaeffer, *J. Ind. Eng. Chem.*, 1912, **4**, 836). Barium

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[1] Samples containing chlorosulphide substitutes must be first treated with alcoholic potassium hydroxide as already described, and the chlorine estimated as above in the residue.

[2] The use of platinum crucibles for this estimation should be avoided in all stocks containing lead, owing to the danger of damage to the platinum by the lead during the fusion.

[3] A similar method has been proposed for the estimation of the total sulphur in rubber, the sulphate in the filtrate being precipitated by barium chloride. The results obtained are, however, according to Tankard (Allen, 1907, Vol. 2, Pt. 3, p. 314, footnote) quite valueless, a large amount of the sulphur present being volatilised in the form of organic sulphides.

[4] Attention has been called to the possibility of antimonial contamination of aerated waters by the red rubber rings used in some kinds of bottles. The insoluble form in which antimony occurs in rubber makes it an unlikely impurity except in traces (which have indeed been found in certain waters).

sulphate (when present) will, of course, remain insoluble in hydrochloric acid with the siliceous portion of the mineral matter, and may be separated from the latter by fusion with alkali carbonates in the usual way.

**Carbonic acid** in the mineral matter (which frequently occurs as calcium and magnesium carbonates, less frequently as lead and zinc carbonates) may be estimated in vulcanised rubber articles, by treating the finely rasped sample (cutting will not suffice) in a Geissler or similar apparatus with dilute hydrochloric acid in which a small quantity of cupric sulphate has been dissolved. The latter serves to retain the hydrogen sulphide evolved from any sulphides which may be present. In the case of non-vulcanised rubber, the caoutchouc must be removed (wholly or partly) by treatment of the sample with boiling nitrobenzene, and a portion of the powdered residue treated as above.

Another method for carbonates is given below. The hydrogen sulphide is oxidised by the sulphuric acid and dichromate mixture and does not interfere with the accuracy of the procedure.

**Carbonates.**—The estimation of the carbonates is accomplished by treating 1.00 grm. of finely ground rubber with hydrochloric acid, and absorbing the carbon dioxide in soda lime tubes. The arrangement of the tubes in the absorption chain is (*a*) (*b*), conc. sulphuric acid and potassium dichromate, (*c*) (*d*), soda-lime tubes; (*e*) conc. sulphuric acid and potassium dichromate, of the same concentration as that in tube (*b*). Tubes (*c*) (*d*) and (*e*) are weighed.

In the case of rubbers containing carbonates and sulphides, these constituents may be estimated separately as already described, or by estimating the total gases (by loss) given off when the finely divided sample is treated with hydrochloric acid in the usual manner, and subtracting the hydrogen sulphide evolved (previously found). The difference represents the carbon dioxide in the sample.

For the estimation of the *sulphides of antimony and mercury*, when occurring either alone or together in a sample of rubber, the method described by Frank and Jacobsohn (*Gummi-Zeit.*, 1909, **23,** 1046–1047; *cf.* also Collier, Levin and Scherrer, *India Rubber J.*, 1920, **60,** 1297–8) may be followed. The sample, cut up into small pieces, is oxidised, as in the estimation of sulphur, by a double evaporation with nitric acid. Potassium chlorate is then carefully

added, and evaporation with nitric acid on the water-bath repeated several times.   Finally the nitric acid is driven off by evaporation with hydrochloric acid, the residue taken up with the latter acid, the solution diluted with water and filtered hot.   If unoxidised organic material should render filtration difficult, the sample is oxidised by repeated heating with fuming nitric acid and potassium chlorate in an Erlenmeyer flask.   As a rule, however, this is not necessary.   Insoluble mineral constituents remain on the filter and are estimated by incineration.   The antimony and mercury are precipitated from the hot filtrate—after most of the acid has been driven off, and ammonium chloride added to assist precipitation —by hydrogen sulphide.   The mixed sulphides are collected on a weighed filter, or in a Gooch crucible, washed in turn with alcohol, ether, carbon disulphide and ether, to remove free sulphur, dried, and weighed.   The antimony sulphide is then removed by means of ammonium sulphide, and the mercury sulphide washed as before, dried, and weighed.   If necessary, the antimony in the filtrate may be converted into tetroxide, by evaporation and oxidation with nitric acid, and weighed as such.

If other minerals be present in the same sample they may be estimated in the usual way in the filtrate from the mixed sulphides.

Wagner's method (*Chem. Zeit.*, 1906, **20,** 638) for the estimation of antimony in vulcanised rubber is carried out as follows:

0.5 to 1.0 grm. of the finely divided sample is mixed in a porcelain crucible with about 5 times its own weight of a mixture of sodium nitrite and potassium carbonate (1:4).   A layer of the mixture is also placed on the top.   Heat is cautiously applied, and gradually increased until the mass fuses.   Any particles of carbon remaining are oxidised by addition of potassium nitrate.   The cover of the crucible should be kept on during this process.   The mass is allowed to cool, dissolved in water, boiled with excess of hydrochloric acid to expel nitrous acid, filtered, and the antimony precipitated from the filtrate by means of hydrogen sulphide.   If other metals be present the antimony sulphide is dissolved, after filtration, in ammonium sulphide and reprecipitated by hydrochloric acid.   The sulphide is then collected on an asbestos filter, dried in a current of carbon dioxide and weighed as $Sb_2S_3$.

**Ebonite.   Vulcanite.**—When the proportion of sulphur employed in vulcanising rubber is very large (*e. g.*, 30%) and the

articles are heated for a longer time and (or) at a higher temperature than necessary for the production of ordinary vulcanised rubber, a plastic mass is obtained which, on cooling, possesses the consistence of horn, and can be turned and worked in the same way. This product forms the vulcanite or ebonite of commerce; sometimes it is referred to simply as "hard rubber."

Ebonite and similar hard-rubber products frequently contain certain resins (such as shellac and colophony), asphalt and pitch, and other substances in admixture. Fatty and mineral oils are frequently used. According to Heinzerling and Pahl[1] the quality of hard rubber is much deteriorated by the addition of rosin oil and resin, while on the other hand asphaltum increases the strength and elasticity of the product.

**Analysis of Ebonite.**—Whilst highly-vulcanised samples of soft rubber are difficult to dissolve by the nitrobenzene or other process (page 394), hard-rubber goods, such as ebonite, are quite insoluble in any known solvent.

Hard rubbers are not likely to contain any admixture of fatty substitutes, although in addition to rubber and mineral matter, certain resins and pitches are frequently present.

Separate estimations should also be made of the mineral matter and of the sulphur in the mineral matter. The sample is filed to a very fine powder, and about 2 grm. of the well-mixed powder are extracted with hot acetone for 8 hours, in the manner described on page 381.

The acetone extract usually consists largely of sulphur, and this may be estimated by the same procedure as in the case of soft vulcanised goods. When the amount of organic acetone extract (total acetone extract *minus* free sulphur) exceeds 4% of the amount of rubber present it is probable that added resinous substances are present in the sample. The detection of the particular resin or resins present is a very difficult—usually impossible—task.

The residue from the extraction with acetone is next subjected to the action of epichlorhydrin in the extraction apparatus. It is not necessary to dry the residue after extraction with acetone, a flask containing about 75 c.c. of epichlorhydrin being attached to the apparatus as soon as the first extraction is completed. The extraction with epichlorhydrin is continued for about 3 hours. The flask

[1] *Verh. d. Vereins z. Beförd. d. Gewerbefl.*, 1891, 415; 1892, 25. *Cf. J. Soc. Chem. Ind.*, 1892, 11, 530.

must be heated upon a sand-bath or asbestos-coated wire gauze, since epichlorhydrin boils at 117°. Dichlorhydrin may be used instead of epichlorhydrin, but the b. p. of the former is very high (177°), and for this reason epichlorhydrin is the preferable solvent. These two solvents dissolve a large number of resins which are partly or wholly insoluble in acetone, as, for instance, amber, copal, dammar, mastic, shellac, etc. These resins, together with acaroid, benzoin, colophony, elemi, and sandarac, which are soluble in acetone, constitute the chief resinous constituents of hard-rubber goods. Shellac and amber are those most frequently employed. The resins are soluble in alcohol, whilst the waxes and pitches (boiled tar, stearin pitch) are insoluble. The waxes (paraffin-wax, ceresin and ozokerite) are fairly soluble in acetone (page 381), the pitches being partially soluble in acetone and in cold nitrobenzene. Asphaltum and sulphuretted stearin-pitch (Callender's bitumen) are fairly soluble in warm nitrobenzene.

The epichlorhydrin is distilled from a paraffin-bath kept at about 120° to 122°, and the residue finally dried for 2 hours at 110°. Any sulphur present in the extract may be estimated by the method employed for the analysis of the pyridine extract of vulcanised rubber (page 127 in Vol. IV, Fourth Ed.).

Before extracting the matter insoluble in epichlorhydrin with chloroform, the residue should be dried until free from the former solvent. The extraction with chloroform is then carried out as described on page 381.

The *sulphur* in the insoluble residue is next estimated as in the case of total sulphur in rubber (page 400). The figure obtained gives the sulphur of vulcanisation and that present in the mineral matter.

The *bases* present in the mineral matter of the sample are estimated and calculated as follows: Lead is calculated as PbO (litharge), antimony as the pentasulphide, and mercury as sulphide. Zinc may be present as oxide or sulphide; calcium as carbonate, sulphate or hydroxide; barium generally as sulphate, sometimes as carbonate; magnesium as oxide or carbonate. A little of the ebonite powder should be examined by heating with hydrochloric acid (1:3). Any evolution of hydrogen sulphide will probably be due to the presence of zinc or lead sulphides, carbonic acid to the presence of calcium carbonate. The absence of barium from the solution obtained

proves that any of this base present in the sample is in the form of sulphate. The sulphur thus found in inorganic combination is deducted from the sulphur in the insoluble residue F, when the percentage of sulphur of vulcanisation is obtained.[1]

The amount of rubber in the sample is obtained by difference. This is a most unsatisfactory procedure, but it seems to be as good as we can do with our present knowledge.

**Direct Estimation of Rubber in Ebonite.**—Hübener (*Chem. Zeit.* 1909, **33**, 144–145, 155–157, has described a method by which the percentage of rubber in a sample of ebonite may be estimated with comparative ease. On account of the great importance attaching to such a method, if of proved value, a description is given here, though it must be pointed out that the method has not yet been sufficiently discussed to warrant its unconditional acceptance (see also page 400).

0.1 grm. of the finely divided ebonite is covered with about 75 c.c. of water and 10 c.c. of bromine, and kept at a moderate temperature until the action of the bromine is complete, and most of the excess is volatilised. The remaining bromine is then driven off by increasing the temperature. The grey, fluocculent solid is filtered off, and the free sulphur (oxidised to sulphuric acid) estimated in the filtrate by precipitation with barium chloride. The bromine-derivative is transferred to a flask, and heated with 10–15 c.c. of nitric acid (sp. gr. 1.4), free from halogen, in presence of excess (say 25 c.c.) of $N/10$ silver nitrate, until fumes are given off. The liquid is evaporated to about 15 c.c. in bulk, diluted with water, and 5 c.c. of a saturated solution of iron alum added. The excess of silver is estimated by titration with thiocyanate, and the amount of combined bromine calculated from the amount of silver used. The amount of rubber hydrocarbon present is now calculated in the following way. Since, in the treatment with bromine, all double linkages in the rubber molecule not already satisfied by sulphur become saturated with bromine, the water-insoluble precipitate may be assumed to consist potentially of two portions, viz.: (*a*) rubber hydrocarbon completely saturated by bromine, *i. e.*, $C_{10}H_{16}Br_4$; (*b*) rubber hydrocarbon completely saturated by sulphur, $C_{10}H_{16}S_2$. Portion (*a*) is calculated from the amount of combined bromine, portion (*b*) from the sulphur of vulcanisation. The latter is taken as the difference between total sulphur, estimated by one of the ordinary

[1] This method cannot be said to be invariably accurate since zinc and barium may be present in two different forms, and error would thus result in the calculation.

methods, and free sulphur as estimated in the manner described above. When lead, calcium, or barium compounds are present in the ash, these must be estimated quantitatively and the amount of sulphur in the corresponding sulphates must be added to the free sulphur. For these metals are either present as sulphates in the original vulcanised mixing, or are converted into sulphates by the action of the bromine, or of the sulphuric acid formed by its interaction with the free sulphur.

## RUBBER SUBSTITUTES

The manufacture of rubber substitutes (surrogates) has been the subject of innumerable patents. A large number of these so-called substitutes have as their basis, or starting-point, some one or other of the fatty oils, which are oxidised with the formation of solid products ("factice"). Other patents describe the preparation of substitutes for india-rubber from various compositions, containing such substances as leather, cork, asbestos, gelatin and glycerin, and ichthyol oil, with which are generally incorporated linseed oil and waste-rubber. It is very doubtful whether these products have any real commercial value.

**Fatty substitutes (oil substitutes)** for rubber are recognised in commerce in 3 varieties, namely, "white" and "brown" (black) substitutes, and "blown-oil" substitutes. They are generally yellowish elastic substances, with a slight, characteristic odour, and a moist and oily feel. They are insoluble in the usual solvents. "White substitute" is prepared by the action of sulphur monochloride ($S_2Cl_2$) upon the triglycerides of unsaturated fatty acids (linseed, castor, corn, cottonseed and colza oils) in the cold (100 parts oil to about 25 parts of sulphur chloride), and "brown substitute" by the action of sulphur at high temperatures upon similar triglycerides, the oils being used either in the natural state or previously oxidised (blown). Thus white substitute is a chlorosulphide, and brown substitute, a sulphide, of fatty oils. "Blown-oil substitutes" are prepared by the action of air or oxygen upon oils, and they consist therefore of oxidised triglycerides. Oil substitutes do not absorb any considerable amount of iodine, the sulphur chloride forming addition-products and converting the unsaturated fatty acids into saturated compounds (Henriques). Substitutes made from "blown" oils are known in the trade as "floating substitutes"

(because, on account of their low sp. gr., they float on water). Substitutes made from ordinary oils are heavier than water.

R. Henriques (*Chem. Zeit.*, 1893, **17,** 916) has pointed out that since glycerides of the saturated fatty acids are indifferent to sulphur chloride, mixtures of these fats with the ordinary oils would yield substitutes containing comparatively small amounts of sulphur chloride, and such substitutes would give analytical results very similar to those of substitutes prepared from oxidised cotton-seed oil. Boiling alcohol or acetone, however, would extract all the saturated fats from these compound substitutes, while the ordinary substitutes yield nothing to either. Henriques states that saturated and unsaturated glycerides may. possibly be separated by treatment with sulphur chloride, and subsequent extraction with alcohol.

These substitutes are not in any sense real substitutes for natural india-rubber. Their true nature (that of fatty oils) is not changed by the vulcanisation to which they have been subjected; they are still triglycerides and therefore saponifiable. For this reason they cannot withstand many of the conditions to which manufactured rubber articles are subjected, such as high temperature steam, alkalies, etc. These products are therefore simply organic filling-materials or adulterants. Perhaps the word "adulterant" is too strong, for after all the rubber manufacturer uses his raw materials for the purpose of producing an article of predetermined quality at as low a price as possible. At a period of say ten years ago, or at about the time of the fourth edition of this work,, the high cost of rubber led to the use of oil substitutes, as well as of some other materials, largely to reduce raw material costs. At the present writing (1924) rubber is not very much more expensive than some of the oil substitutes, and the continued use of these substances, although in much smaller quantities, draws attention to the fact that the modification of a rubber compound by the addition of certain amounts of oil substitutes gives to the compound new mechanical properties that at times are really desirable.

The proportion of sulphur in the fatty substitutes is very variable, ranging from 5 to more than 17%. The amount of soluble fatty oil and of free sulphur present should be small, whilst when a large amount of free sulphur is present, it must be taken into consideration when the vulcanisation of the mixture of rubber and substitute is to be carried out, or overvulcanisation may result. White

substitutes rarely contain more than traces of free sulphur; oxidised oil substitutes contain neither sulphur nor chlorine. A white substitute should contain not more than 10% of soluble fatty matter and not less than about 8% of combined sulphur; a brown or black substitute should not contain more than 5% of soluble fatty matter, and the proportion of free sulphur should not exceed 40% of the amount of combined sulphur. These figures are only approximate ones.

Similarity in chemical composition between samples of these substitutes does not necessarily imply equal suitability for mixing with india-rubber. The substitute added to rubber forms a kind of solid emulsion with the latter, and the finer the emulsion formed, the better is the substitute. A solution of the consistency of thin honey is obtained by dissolving a small quantity of the mixture in benzene. A small drop of this solution is placed on the end of a microscope slide, and another slide drawn rapidly across it. A thin quickly-drying film of the sample is thus obtained, and on examination under the microscope this should appear as an almost homogeneous mixture. Bad substitutes sometimes form no emulsion at all, but break up into a mass of streaky or scaly flakes.

"Brown" substitute is almost exclusively employed in those goods which are to be vulcanised by sulphur, whereas "white" substitute is generally used for cold-cured goods, *i. e.*, goods vulcanised by sulphur monochloride. Sometimes, as in the case of greyish-white gas-tubing which is "hot-vulcanised," "white" substitute is used for the sake of the colour required, but the practice is liable to be detrimental to the quality of the finished article.

The "brown" substitutes manufactured from natural and from "blown" oils (in the latter case the oil is oxidised until it has a sp. gr. of about 0.960) are equally satisfactory, and the latter variety may be distinctly superior for certain purposes; but, in the case of "white" substitutes, those prepared from "blown" oils are not so good as the natural oil products, the former being somewhat unstable in character.

The analyses on page 411 of various fatty substitutes are given by R. Henriques (*Chem. Zeit.*, 1893, **17,** 634–638):

The results on p. 411 show the composition of these products as obtained from various oils. The methods for the estimation of chlorine, etc., and for the identification of any particular substitute

| | Commercial products | | | | | Linseed oil substitutes from | | Colza oil substitutes from | | Poppy-seed oil substitute from oxidised oil | Castor oil substitutes | | Substitute from oxidised cotton-seed oil |
| | White substitute | | | Brown substitute | | | | | | | | | |
| | A[1] | B[1] | C[2] | A | B | Fresh oil | Oxidised oil | Fresh oil | Oxidised oil | | With minimum of $S_2Cl_2$ | With maximum of $S_2Cl_2$ | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sulphur | 6.4 | 6.17 | 8.25 | 15.48 | 17.71 | 9.34 | 4.78 | 8.28 | 6.59 | 7.68 | 4.82 | 10.6 | 6.23 |
| Chlorine | 5.0 | 5.86 | 8.88 | 0.7 | 0.36 | 8.84 | 4.85 | 7.62 | 5.95 | 7.44 | 6.70 | 8.95 | 5.36 |
| Water | 0.85 | 1.0 | …… | …… | …… | 3.02 | 0.85 | …… | …… | …… | …… | …… | …… |
| Mineral matter (ash) | 0.8 | 5.51 | …… | …… | …… | …… | …… | …… | …… | …… | …… | …… | …… |
| Fatty acids | 90.45 | 73.58 | …… | …… | …… | 79.6 | 81.67 | 86.89 | 87.95 | 74.90 | 85.35 | …… | …… |
| Sulphur in the fatty acids | 6.12 | 6.45 | 8.15 | 14.14 | 15.20 | 9.88 | 4.06 | 8.34 | 6.54 | 8.32 | 5.32 | …… | 6.44 |
| Chlorine in the fatty acids | 0.83 | 0.43 | …… | …… | …… | Trace | 0.60 | Trace | Trace | …… | 0.26 | Trace | Trace |
| Iodine absorption of substitute | 30.9 | 31.0 | 32.6 | 42.0 | 42.0 | 56.3 | 52.6 | 32.5 | 26.9 | 33.6 | 35.2 | 21.9 | 30.3 |
| Iodine absorption of fatty acids | 91.3 | 91.2 | 102.3 | 129.0 | 125.6 | 160.3 | {141.2 / 121.0} | 101.5 | 102.8 | 133.3 | {136.2 / 147.4 / 152.1} | 143.5 | 91.5 |
| Acetyl value | …… | …… | …… | …… | …… | 21.0 | 19.6 | 31.0 | …… | …… | …… | 105.6 | 51.3 |

[1] A and B, manufactured from oxidised oil.   [2] C, from natural oil.

or mixture of substitutes in india-rubber, are given on pages 402 and 403. The iodine absorption of the substitutes and of their fatty acids has been suggested for identifying the oil present. However, the practice of using two or more oils in the preparation of these substitutes renders such a procedure practically worthless.

For the examination of the fatty substitutes as to their suitability for manufacturing purposes in admixture with india-rubber, the more important estimations are the free and combined sulphur, soluble fatty oil, and ash.[1] Acetone is the best solvent to employ, and 3 to 5 grm. of the sample are extracted in a Cottle apparatus for 4 hours with this solvent. The acetone is evaporated from the extract, and the residue redissolved in cold acetone, when the fatty matters will in some cases dissolve, leaving the sulphur in crystals, and almost insoluble. The liquid can be filtered to get rid of the fatty matters, and the free sulphur and fatty matters may then be weighed separately. In other cases it will be found necessary to oxidise the complete acetone extract, since some lightly vulcanised oil which is only sparingly soluble in cold acetone may be carried through with the free oil and sulphur into the extract. The method of procedure in these cases is the same as that described on page 381.

As the fatty matters extracted by acetone contain a certain proportion of combined sulphur, if the amount of free sulphur found by simple separation with acetone, as above, be deducted from the total sulphur of the sample, the result is in excess of the truth, since only the sulphur combined in the insoluble substitute is reckoned as combined sulphur. The latter figure is therefore estimated directly in the acetone-extracted substitute. The same methods are employed as described on page 381.

The character of the fatty acids obtained from a fatty substitute or, in the case of rubber, isolated from the alcoholic soda extract gives a clue to the kind of substitute under examination. Thus the fatty acids from oxidised oil substitutes never contain more than traces of sulphur and chloride, the substitute itself rarely containing sulphur or chlorine in amounts exceeding 0.5%. Brown (sulphide) substitutes contain usually from 4 to 9% of sulphur, the whole of which is found in the fatty acids when isolated. Only traces, at most, of chlorine are present in brown substitutes or their fatty acids. The fatty acids of white (chlorosulphide) substitutes

[1] An estimation of the ash is frequently of much value, for a number of samples of oil substitutes have been "loaded" with cheap mineral fillers, usually clay or whiting. This is pure adulteration, and is to be condemned most strongly.

contain the whole of the sulphur of the substitute, but the greater part of the chlorine is found in the alcoholic sodium hydroxide liquid on saponification. It may be estimated in this alkaline solution as described on page 388.

In certain cases the kind of substitute or substitutes can only be determined with difficulty. It has already been pointed out that when a chlorosulphide substitute has been used in a hot-vulcanised article, a large proportion of the chlorine is evolved as hydrogen chloride, and combines with the rubber of the sample, so that it is not found with the sulphur in the saponification liquors. In such a case, the substitute present may be erroneously regarded as a sulphide substitute. Estimation of the sulphur and chlorine of vulcanisation should next be made. If the rubber does not contain sufficient chlorine to be about equal to the sulphur in the alcoholic sodium hydroxide extract, the substitute present must be a sulphide (brown) substitute.[1] Cold-vulcanised (sulphur chloride) goods never yield more than mere traces of free sulphur to acetone, whilst sulphide substitutes and hot-vulcanised rubber goods contain amounts of free sulphur which will readily be detected in the acetone extract.

## RECLAIMED RUBBER

"Recovered," "regenerated," or reclaimed rubber is made from cuttings and scraps which compose the factory wastes or from worn out rubber articles. There are three general types of processes.

*Acid Process.*—The acid process is used almost exclusively in reclaiming unvulcanised scrap containing fabric. A wooden or lead lined tank is used, the scrap is placed in a vat, dilute sulphuric acid added, and heat applied through steam coils. The temperature range is from 65–95°; the time from 8 to 24 hours. Much depends upon the character or the stock, which dictates the temperature which may be used, and hence the time required. The acid is drained off, the rubber washed in the usual rubber washing mill, dried (usually in vacuum driers), and milled into rolls or slabs. The cuttings from tire fabrics are reclaimed in this manner, the product being known usually as "reclaimed friction."

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[1] Only thin rubber surfaces are capable of being vulcanised by the cold process, so that when a rubber article of any thickness contains chlorine, it suggests the presence of a chlorosulphide substitute.

The acid process removes the cotton, and part of such fillers as are readily soluble in the acid (such as whiting, zinc oxide, etc.). The free sulphur is practically unchanged.

*Alkali Process.*—In the alkali process, frequently known as the Marks process, in honour of the inventor, the finely ground vulcanised rubber, which may or may not contain fabric, is treated with caustic alkali solutions in an autoclave at fairly high temperatures, usually around 150°. The rubber is washed, dried and milled into slabs or rolls. The cotton is destroyed, the final traces being removed in the washing. Some of the fillers are attacked, but probably less so than in the acid process. Most of the free sulphur is removed, but a part of it combines with the rubber, so that the vulcanisation coefficient, *i. e.*, the percentage of combined sulphur to rubber, is higher in the reclaimed rubber than in the scrap from which it was made. The alkali should be completely removed on account of its effect on subsequent vulcanisation. In the milling, oils are frequently used as softeners. In some cases the oils may be introduced into the rubber during the devulcanisation process, but in this case the oils must be of the paraffin type, as fatty and animal oils are saponified and removed during the washing.

*Mechanical Process.*—The mechanical process consists in taking finely ground vulcanised scrap, which should be practically free from fabric, mixing it with oils, in the proportion of from 10 to 25 parts of oil to 100 parts of rubber, placing in pans 6 to 10″ deep, and heating in live steam at 75 to 125 lbs. steam pressure for a period of from 8 to 24 hours. On cooling, the product is usually milled into slabs about half an inch thick. It is sometimes dried before milling, but usually the moisture content is reduced to practical limits during the milling operation. The yield is practically 100% of the total weight of the rubber and oils. The oils used are the pine tar oils, coal tar residues, rosin and rosin oil, corn oil, cottonseed oil, mineral oils, and petrolatum. Practically all the free sulphur combines with the rubber during the devulcanisation process, as might readily be inferred from the manner of heating.

Such reclaimed rubbers are usually inferior to alkali reclaims, but find extensive use in mechanical goods, rubber heels, soles, etc.

*Uses of Reclaimed Rubber.*—The reclaimed friction is almost as good as the rubber compound from which it is made, being usually

a bit softer. It finds ready use in the tire frictions and skim stocks, particularly when a manufacturer reclaims his own scrap. The free sulphur content is normally rather high, and must be taken into account, particularly in such stocks as are expected to be non-blooming. The alkali reclaims are inferior to the stocks from which they are made, but find extensive use not only because of their cost, but because at times they add peculiarly desirable qualities to the stocks of which they form a part. The mechanical reclaims have only their low cost to recommend them.

The proportion of rubber in reclaims varies from 25 to 85%, but is usually around 40%, the higher percentages being found in the so-called "floating reclaimed frictions," and in the pure gum tube reclaims.

The analysis of reclaimed rubber is carried out by the same methods as described under *Vulcanised Rubber*. The quantity and nature of the acetone extract are useful data in judging of the value of samples of reclaimed rubber. Calculated upon the india-rubber of the sample, good reclaimed rubber should give an acetone extract below 10%, although many commercial samples will be found to give 20–30%. The smaller the amount of extract, the better the sample. The presence of saponifiable oils in the acetone extract should be ascertained by the Koettstorfer process. Since the kind of fatty oil present is usually unknown, a mean saponification value of 190 may be taken for the purpose of calculation, when the percentage of fatty oil is obtained by the formula

$$\frac{100 \times \text{KOH required in milligrm.}}{190 \times \text{grm. of acetone extract taken.}}$$

The physical characters of the residue from the acetone extraction are important. Many commercial samples after extraction leave a residue consisting of a crumbly mass of rubber, etc., which has practically no elasticity or plasticity. A good sample will leave an appreciably plastic residue. Reclaimed rubber which loses by extraction with acetone any valuable property it may have possessed is only useful as a "filling" material for mixing with india-rubber.

The cold nitrobenzene process for the detection of asphaltum may be used in the analysis of reclaimed rubber after the acetone extraction has been carried out, or the chloroform extract may be made. Either test is only qualitative. Fatty substitutes are

estimated by the alcoholic potassium hydroxide process (page 383). To estimate accurately the sulphur of vulcanisation in a sample of reclaimed rubber, use the same method as for vulcanised rubber.

When rubber has been subjected to a high temperature (say 150°, or higher) during the process of recovery, it may be regarded as probable that the rubber itself will have been affected by the high temperature, and products of decomposition formed. Weber has suggested a method for the estimation of such products in reclaimed rubber by isolating them as bromine derivatives. These brominated decomposition products (containing over 60% of Br) are insoluble in alcohol and very sparingly soluble in benzene, whereas the bromine derivatives of the oils present in recovered rubber are readily soluble in alcohol and benzene and mixtures of these two solvents. For the purpose of estimating these products, Weber dissolves the acetone extract (containing oils and decomposition products of rubber) in a mixture of 2 parts of benzene and 1 of absolute alcohol, and adds bromine in slight excess to the solution. The bromine compounds of any decomposition products present are precipitated and can be filtered off. The precipitate is washed first with the mixed solvents and finally with alcohol, and then dried at 50°. Weber found that in 8 samples of reclaimed rubber the percentage of bromine in the compound obtained varied from 62.5 to 67.1, so that it is necessary to estimate the bromine in the compound obtained and subtract the weight found from the total weight of the precipitate. The percentage of decomposition products can then be calculated. Three reclaimed rubbers examined by Weber, which had been prepared from the same rubber scrap with mineral oil at temperatures of 140°, 160°, and 185°, gave, respectively, the following percentages of decomposition products: 1.16; 1.86; 2.53%. The process is likely to prove useful when the cause of the deterioration of any sample of manufactured india-rubber is to be investigated.

## GUTTA-PERCHA

Gutta-percha occurs in the *latex* of various trees belonging to the *Sapotaceæ* (e. g., *Palaquium pustulata* and other species), growing in the Malay peninsula and archipelago. It is called "percha" by the natives, "gutta" being the Malay name for gum.

The extraction and purification of gutta-percha have been fully described by E. F. A. Obach (Cantor Lectures, *J. Soc. Arts*, 1897 and 1898; *J. Soc. Chem. Ind.*, 1898, **17**, 470).[1]

The crude gutta-percha of commerce is a reddish, marbled mass, which often contains sand, pieces of wood, bark, etc. It is said that plastic gum, probably *balata*, is sent from London to Singapore to be mixed with the gutta-percha. The commercial product is certainly very frequently and largely adulterated. Gutta-percha is purified by thoroughly washing the fine shavings with cold and hot water, and then kneading them into blocks. The product obtained by extracting the leaves, twigs, etc., of the gutta-percha tree is much purer than the ordinary commercial gutta-percha.[2]

Gutta-percha dissolves in all the solvents of india-rubber. It is hard, tough, and slightly elastic at the ordinary temperature, becomes pliable at 25°, and gradually softens on heating. When pure it has a sp. gr. of about 0.961. At 60° it is so plastic that it may be pressed into any shape or drawn into threads. It becomes adhesive at 100°. When boiled in water, it swells up somewhat and takes up about 5 to 6% of water, but loses this gradually on subsequent exposure to air. When exposed to air and sunlight, gutta-percha absorbs oxygen like caoutchouc, and becomes brittle. Gutta-percha is also quickly acted upon by ozone. It can be preserved in the dark or under water, especially sea-water, without undergoing any alteration. It is not attacked by alkalies nor by hydrofluoric acid, which is therefore frequently stored in bottles made of this substance. Gutta-percha is a non-conductor of electricity.

Unlike india-rubber, gutta-percha has a cellular structure, which becomes fibrous when subjected to tension. It is very porous, and hence many adulterated specimens, which have a true gravity of more than 1.00, actually float on water.

The action of nitrous anhydride ($N_2O_3$) upon gutta-percha is similar to its action upon rubber, the nitrosite, $C_{10}H_{15}N_3O_7$ (Harries' "nitrosite C."), being apparently formed. Balata also gives a nitrosite closely resembling "nitrosite C." in its chemical characters.[3]

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[1] According to Eng. Patent, 1896, No. 19046, the crushed stems, leaves, and twigs are extracted with light petroleum. Melted paraffin wax may also be used for the extraction. Ramsay, (Eng. Patent, 1897, No. 17936) substitutes rosin oil for the toluene usually employed (Eng. Patent, 1896, No. 654).

[2] On a small scale, gutta-percha may be obtained pure and colourless by extracting it with boiling alcohol, dissolving the residue in chloroform or hot benzene, decolorising the solution with animal charcoal, and then precipitating with alcohol.

[3] See Caspari, *J. Soc. Chem. Ind.*, 1905, **24**, 1274.

By mixing it with sulphur and heating, gutta-percha, like rubber, may be vulcanised, and with large proportions of sulphur it yields a substance resembling ebonite. Gutta-percha is often mixed with rubber in various proportions to increase its elasticity.

Gutta-percha is largely employed for the insulation of electric wires and cables; as a filling and setting for teeth; and for surgical purposes, in the form of gutta-percha tissue. A solution of gutta-percha in chloroform, known as *"traumaticin,"* is used as a substitute for collodion.

The composition of gutta-percha is exceedingly complex, and present knowledge of its chemistry is very imperfect. Payen in 1851 found gutta-percha to contain *gutta, alban*, and *fluavil*. More recently H. Bornträger (*Zeit. anal. Chem.*, 1900, **39,** 502) found alban to consist of several distinct substances. The "albans" and "fluavils" are oxidation products of gutta.

"Gutta" has the empirical formula $C_5H_8$, but is probably a mixture of several polymers of this ultimate composition. On dry distillation gutta yields *isoprene*, $C_5H_8$, and two hydrocarbons of higher b. p., probably containing $C_{10}H_{16}$ and $C_{30}H_{48}$. According to Ramsay, Chick, and Collingridge (*J. Soc. Chem. Ind.*, 1902, **21,** 1367), no compound of the formula $C_{10}H_{16}O$ is obtainable by the direct action of chromic acid on gutta, though such a substance results, with others, from the treatment of alban with oxidising agents.

Commercial gutta-percha contains from 40 to 85% of gutta. At ordinary temperatures gutta is white and soft but not elastic, while at 45° it becomes yellow and pasty, and at 100° to 110° softens, melting and boiling at 130° with decomposition. Gutta is soluble in chloroform, toluene, and carbon disulphide, but insoluble in absolute alcohol, and in ether after treatment with alcohol. Gutta oxidises in the air, and hot nitric acid decomposes it, formic acid being among the products of the reaction.

"Alban" is described as a mixture of white resins, soluble in hot alcohol. A crystalline substance containing $C_{17}H_{26}O$ and a resinous substance of the formula $C_{17}H_{28}O$ have been recognised, and a third constituent is also stated to be present. (See also A. Tschirch, *Arch. der Pharm.*, 1903, **241,** 481; cf. *J. Soc. Chem. Ind.*, 1903, **22,** 1250).

"Fluavil," $C_{40}H_{64}O_2$ (?), is a yellow amorphous resin, which softens at about 50° and boils at 105°. It dissolves in cold alcohol in which the alban resins are practically insoluble.

Work by Tschirch and Müller (*Arch. der Pharm.*, 1905, **243**, 114) goes to show that the 3 "albans" of gutta-percha from New Guinea are distinct from those of the Sumatra product, whilst "fluavil" is apparently a mixture of 2 compounds of different m. p. Tschirch describes the albans as compounds soluble in boiling alcohol, the fluavils as soluble in cold alcohol, and the "albanans" as insoluble in both hot and cold alcohol. India-rubber is stated to contain alban-like substances.

The following figures, showing the composition of commercial gutta-percha and balata, are given by E. F. A. Obach (*J. Soc. Arts.*, 1897 and 1898; *J. Soc. Chem. Ind.*, 1898, **17**, 470).[1]

| Description of material | Percentage composition | | | |
|---|---|---|---|---|
| | Gutta | Resin | Dirt | Water |
| **Raw Gutta-percha** | | | | |
| Range........................ | 23.1 to 84.3 | 10.1 to 65.2 | 1.8 to 22.3 | 1.0 to 26.7 |
| **Cleaned Gutta-percha** | | | | |
| Range........................ | 24.4 to 88.8 | 11.2 to 67.4 | 0.9 to 2.0 | 0.5 to 2.3 |
| Sample A..................... | 78.1 | 19.2 | 1.5 | 1.2 |
| Sample B..................... | 57.5 | 40.9 | 1.0 | 0.6 |
| Sample C..................... | 52.2 | 45.4 | 1.5 | 0.9 |
| Sample D..................... | 55.6 | 40.9 | 1.8 | 1.7 |
| **Hardened Gutta-percha** | | | | |
| Medium quality, cleaned only...... | 54.7 | 39.4 | 2.7 | 3.2 |
| Same sample after hardening...... | 93.0 | 2.8 | 2.5 | 1.7 |
| **Balata** | | | | |
| Raw; average.................... | 43.0 | 39.6 | 10.0 | 7.4 |
| Cleaned; average................ | 52.1 | 47.9 | ............ | ............ |

The following figures show in fuller detail the approximate range of composition of commercial gutta-percha, according to the results of various observers: Water, 1.0 to 1.5%; dirt (woody fibre and soil) 3 to 5%; pure gutta, 30.5 to 83.5%; "alban," 7.0 to 44.5%; and "fluavil," 3.0 to 21.0%. The ash of gutta-percha rarely, if ever, exceeds 0.5%.

W. G. Berry (*J. Soc. Chem. Ind.*, 1904, **23**, 529) has published figures showing the acid and ester values of the resins of gutta-percha and allied substances.

The chief data for the valuation of gutta-percha are to be found in the percentage of moisture, the amount of pure gutta, and the proportion of impurities, such as dirt, etc. The larger the proportion of gutta in a sample (and therefore the smaller the amount

[1] Other analyses of gutta-percha from various botanical sources have been published by V. Romburgh and T. de Haas (*J. Soc. Chem. Ind.*, 1903, **22**, 752). See also *J. Soc. Chem. Ind.*, 1904, **23**, 552 for further figures.

of resin), the more valuable it is for commercial purposes. For the insulation of telegraph cables an article containing not less than 65% of gutta is required. It is stated, however, by W. A. Caspari that the resin of gutta-percha is the insulating constituent and that it is the aim of the insulated-wire maker to obtain a product containing this resin with sufficient gutta to give the desired mechanical properties.

**Balata** is obtained from the latex of *Mimusops balata*, a tree growing in Guiana and Brazil. The commercial product forms a leathery mass and contains oxygen. Balata has a sp. gr. of 1.044 and melts at 149°. It contains "alban" and fluavil," and thus resembles gutta-percha. The pure hydrocarbon separated from balata is isomeric with those from gutta-percha and india-rubber, and, like them, can be vulcanised. Balata is, at ordinary temperatures, somewhat elastic, but becomes plastic on heating (at 50°) like gutta-percha. The composition of raw and cleaned balata is given on page 419.

Formerly balata was employed for coating telegraph wires, surgical instruments, etc. The production of balata has recently decreased, owing to the fact that the tree, which grows in very unhealthy districts, is no longer cultivated and is slowly dying out.

**Analysis of Gutta-percha.**—For the analysis of *gutta-percha*, Marckwald and Frank (*Zeit. angew. Chem.*, 1902, 1029) recommend that 2 grm. of the dried sample should be dissolved in 15 c.c. of chloroform, and the clear solution poured gradually, with constant stirring, into 75 c.c. of acetone. The *gutta* forms a voluminous porous cake, which can be pressed out, washed with acetone without loss, dried at 100°, and weighed. The dirt and insoluble matters, if not previously separated, may be estimated by passing the solution and washings through a tared filter. Any small particles of gutta separated by the filter may be dissolved in hot toluene and added to the main portion.

Alcohol cannot be substituted for acetone in the above process, but good results are obtainable by dissolving 2 grm. of gutta-percha in 10 c.c. of chloroform and adding 100 c.c of ether. After standing for 24 hours, the precipitated gutta is filtered off.

H. Bornträger (*Zeit. anal. Chem.*, 1900, **39,** 502) boils 1 grm. of the sample of gutta-percha for 12 hours under a reflux condenser with 50 c.c. of benzene, filters from dirt, etc., and washes the residue

with hot benzene. The filtrate and washings are then evaporated to 50 c.c., and mixed with 100 c.c. of absolute alcohol. After standing on the water-bath for some hours the *gutta* is completely precipitated, and is filtered off, washed 3 times with hot alcohol, dried at 100°, and weighed. For the separation of the resins, the filtrate should be evaporated nearly to dryness, and the residue taken up with 50 c.c. of boiling absolute alcohol. The solution is transferred to a weighed capsule or beaker, and allowed to stand in the cold for 24 hours. The liquid, containing the fluavil in solution, is decanted, and the residue of "*albans*," well washed with cold alcohol, dried at 80°, and weighed. The "*fluavil*" can be recovered by evaporating the alcoholic solution and drying the residue at 80°, but loss is liable to occur from volatilisation.

Probably current practice today for the analysis of gutta-percha and balata is best represented by the method outlined below: (*India Rubber Journal* 1922, **64**, 179–80).

*Moisture.*—Carefully cut into strips, 5 grm. of the sample, dry *in vacuo* at 95° C. to constant weight.

*Resins.*—Extract 2 grm. of the shredded sample with acetone in a Cottle extractor, for 10 hours, and dry the residue at 110° to constant weight.

*Dirt.*—Extract 5 grm. of the shredded sample with naphtha or toluene; filter off the insoluble matter and weigh.

*Separation of Resins.*—Dissolve in hot alcohol, filter, let the beaker stand 4 hours, filter again, and wash with small quantity of cold alcohol. The insoluble residue contains "albans," and the filtrate contains "fluavil." Each group is transferred to a tared flask or beaker, the alcohol removed, and the residues dried at 90° to constant weight.

**Chicle** is the thickened latex of *Achras sapota L.* and is obtained chiefly from Mexico. It is used as a constituent of chewing-gum. It should be noted that while chicle has little use other than the manufacture of chewing gum, by no means does all chewing gum contain chicle. Resins from various grades of wild rubbers frequently replace entirely the chicle gum.

Chicle is a mixture of water-soluble gum, resins, gutta, and mineral constituents.

According to Prochazha and Endemann (*J. Amer. Chem. Soc.*, **1**, 50–62), the following is a detailed analysis of the dry, cleaned chicle:

```
Arabin...................................... 10.0
Calcium.....................................  9.0
Sugar.......................................  5.0
Water-soluble salts of Ca, Mg, and K........  1.0
    Total soluble in boiling water..................... ——25.00
```

```
Alban....................................... 33.75
Fluavil..................................... 22.50
Hydrocarbon (gutta) soluble in ether........  6.00
                   insoluble in ether....... 12.75
    Total constituents insoluble in water............ ——75.00
```

**Treatment with Solvents.**—The gum may be precipitated from aqueous solution by means of alcohol. When quickly filtered, washed with alcohol and then with ether, and evaporated in a vacuum desiccator, protected from the light, 9% yield of gum is obtained. The reactions of the gum are as follows:

Test for carbohydrate with naphthol-sulphonic acid should show the presence of carbohydrates. Furfural should also be found present when tested with aniline acetate (see Vol. I, p. 258). The gum is optically active.

The residue from boiling water is boiled for several hours in a flask with return flow condenser with alcohol and filtered, when still hot. The alcohol is coloured brown. On cooling, crystals of alban separate to the extent of about 10%. If this treatment is repeated a large number of times, more alban or varieties of the same are extracted and the alcoholic extracts become colourless. The residue is finally soluble in chloroform and may be purified by crystallisation from boiling ether.

# THE CONSTITUENTS OF ESSENTIAL OILS; AND ALLIED SUBSTANCES

By ERNEST J. PARRY, B. Sc., F. I. C., F. C. S.

## (A) HYDROCARBONS

Of the hydrocarbons occurring as constituents of the essential oils of plants, by far the most abundant and numerous are the *terpenes* and their immediate allies. The properties and chief sources of these hydrocarbons will be fully described in the sequel. *Paraffins* occur in a few cases only. Thus the "principal hydrocarbon" of the oil of *Pinus sabiniana* (California) is identical with *normal heptane*, $C_7H_{16}$. The stearoptene or solid portion of oil of rose appears to consist of the paraffin *hexadecane*, $C_{16}H_{34}$, mixed with other substances. The hydrocarbons of the *benzene* series are only rare constituents of the essential oils, with the exception of *cymene*, $C_{10}H_{14}$. *Cinnamene* or *styrene*, a hydrocarbon having the constitution of a *phenylethylene*, $C_6H_5.CH:CH_2$, occurs in small proportion in liquid storax, and other aromatic balsams.

By far the most numerous and important of the hydrocarbons of essential oils are the polymers of *pentine*, $C_5H_8$. The relationship existing between these hydrocarbons is shown by the following arrangement, which is substantially that of Wallach:

A. **Pentines or hemiterpenes,** $C_5H_8$; as isoprene and valerylene.

B. **Dipentines or terpenes,** $(C_5H_8)_2$ or $C_{10}H_{16}$ including pinene, limonene, fenchene, camphene, phellandrene, etc.

C. **Tripentines or sesquiterpenes,** $C_{15}H_{24}$; as cedrene and cubebene.

D. **Diterpenes,** $C_{20}H_{32}$; as colophene and copaivene.

E. **Polyterpenes,** $(C_5H_8)_n$; as the polyprene of caoutchouc.

The above, however, gives no indication of the constitutional relationships between these hydrocarbons. The work of W. H. Perkin, Jr., has, in conjunction with that of Wallach and others made

clear many of these relationships which were till recently very obscure.

The typical hydrocarbon upon which the present nomenclature of the terpenes is based is hexahydro-*p*-cymene which is termed *p*-menthane, and has its carbon atoms numbered as follows:
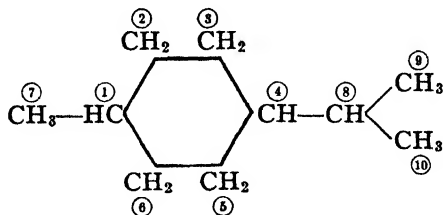


The usual rules of chemical nomenclature are followed so that the following examples are easily understood:
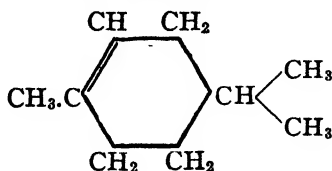


Containing one double linkage is $\Delta^1 p$—menthene. Limonene is $\Delta^{1.8-9}$-*p*-menthadiene, of the formula
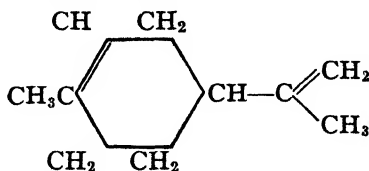


The corresponding alcohols, and the *ortho-* and *meta*-compounds follow the same rules of nomenclature.

### Pentines. Hemiterpenes

Eight compounds of the composition $C_5H_8$ can theoretically exist, assuming that the formulæ are all open chains.

**Isoprene,** which is the most interesting of the hemiterpenes, has the constitution of a $\beta$-methyl-crotonylene (*i. e.,* unsymmetrical methyl divinyl), $CH_2:(C.CH_3).CH:CH_2$, and hence belongs to the acetylene series (see Vol. 3). It is obtained, together with other products, by the dry distillation of caoutchouc and gutta-percha.

It is a volatile liquid boiling at about $37°$, and is not affected by treatment with mercuric bromide and water. By careful management, W. A. Tilden obtained from isoprene a tetra-bromide, $C_5H_8Br_4$, as a yellowish, oily liquid which was decomposed on distillation. When isoprene is heated to about $280°$ for some hours it polymerises with formation of *dipentene*, $C_{10}H_{16}$, and colophene, $C_{20}H_{32}$. Isoprene behaves similarly with sulphuric acid, yielding a terpene and a fluorescent colophene.

On exposure to the air, isoprene absorbs oxygen and becomes converted into a white, syrupy substance, which on distillation suddenly changes, often with explosive violence, into a white amorphous mass of the composition $C_{10}H_{16}O$. Another characteristic reaction of isoprene is that of being converted into true caoutchouc or india-rubber when brought into contact with certain chemical agents, such as strong hydrochloric acid or nitrosyl chloride. Tilden has also observed the spontaneous polymerisation of isoprene (obtained from turpentine oil) into india-rubber, the inducing cause being possibly the formation of acetic or formic acid by the oxidising action of the air, the acid thus produced converting the remainder of the isoprene into caoutchouc, a reaction that would be of great commercial importance if isoprene were more readily obtainable.

**Styrolene,** or phenyl-ethylene, $C_8H_8$, is an aromatic oil found in storax and some other balsamic substances, and is prepared artificially by heating cinnamic acid with caustic lime. Its characters are as follows:

Sp. gr. at $15.5°$. . . . . . . . . . . . . . . . . . . . . . . . . . . . . . $0.907$
Ref. index at $20°$. . . . . . . . . . : . . . . . . . . . . . . . . . . . $1.5403$
B. p. . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . $140°-145°$

It yields two types of halogen derivavites, the $\omega$ and the $\beta$ series. The latter are useless in perfumery, but the $\omega$-substances are of importance. The $\omega$-bromo derivative, $C_6H_5.CH:CHBr$, is a crystalline substance melting at $7°$ and boiling at $220°$. It possesses a powerful odour of hyacinths and forms the basis of many perfumes of this particular type.

### Cymene, $C_{10}H_{14}$; or, $C_6H_4(CH_3)(C_3H_7)$

Cymene is a member of the benzene series of hydrocarbons, and has the constitution of a *methyl-isopropyl-benzene*. It cannot be

made to combine with hydrogen to form terpenes, though the converse action can generally be effected by careful oxidation of the terpene with iodine.

$p$-Cymene is the principal constituent of the oil from wild thyme (*Thymus serpyllum*), in which it occurs with thymol and smaller quantities of carvacrol and a terpene.   Cymene is present in smaller proportion in the essential oils of ginger, nutmeg, citron, ajowan, cumin, thyme (*T. vulgaris*), sage, *Origanum creticum* and *Satureja hortensis* (pepper-wort).   It also occurs in resin spirit and in old oil of turpentine.   It was first obtained from Roman cumin oil (*cuminum cyminum*) in which it occurs with *cuminol* or *cumic aldehyde*, $(CH_3)_2CH.C_6H_4.CHO$, and from which it derives it name.   It may be conveniently prepared by mixing camphor and phosphorus pentoxide in molecular proportions and heating gently till action commences $(C_{10}H_{16}O+P_2O_5=C_{10}H_{14}+2HPO_3)$.   The flask is then cooled, the cymene poured off from the metaphosphoric acid, heated again with phosphorus pentoxide, and then distilled several times over sodium.   Fenchone under similar conditions is converted into the isomeric *m-cymene*.   *o*-Cymene has not been found in essential oils or in their reaction products.

$p$-Cymene is also formed in considerable quantity by treating turpentine oil with sulphuric acid, and still more abundantly (together with ether) by heating turpentine oil with ethyl sulphate (*Compt. rend.*, 1880, 90, 1428).

$p$-Cymene is a colourless, strongly refracting fluid, having an agreeable odour, recalling that of oil of lemons.   It boils at 175° to 176°, and has a sp. gr. of 0.86 at 15°.   When boiled in a flask for 30 or 40 hours with a large excess of strong chromic acid mixture, or until the liquid dropping from the inverted condenser no longer appears oily, cymene is oxidised with formation of acetic, paratoluic, and terephthalic acids.   To detect the last product, which is characteristic, the contents of the flask are diluted with water and thoroughly cooled.   The insoluble terephthalic acid is filtered off, and purified by solution in ammonia, boiling with animal charcoal, and reprecipitation by hydrochloric acid.   It is insoluble in water, alcohol, ether, chloroform, or acetic acid.   It sublimes without fusing.   Heated with excess of soda-lime, it yields benzene and a carbonate.

According to C. R. A. Wright, the presence of cymene in an essential oil may be detected by mixing it very gradually with twice its

volume of strong sulphuric acid, so as to avoid all heating. After standing 24 hours the acid is diluted with water, and the oily liquid separated and distilled in a current of steam. If the oily portion of the distillate blackens when shaken with sulphuric acid, the above treatment should be repeated. The product is then oxidised by chromic acid mixture (see above), when terephthalic acid will be obtained if cymene be present.

Cymene has recently assumed considerable commercial importance, an account of the fact that it is obtained in quantity from the crude hydrocarbon oil yielded during the sulphite pulping process by the spruce wood employed, and that from it thymol can be synthesised. Phillips and Gibbs (*J. Ind. Eng. Chem.*, 1920, **12**, 733) give the following details as to its preparation. The crude oil is allowed to stand in contact with lime for about a week, and is then steam distilled. To the distillate a fourth of its volume of sulphuric acid is added, and the mixture (kept cold) mechanically stirred for two hours. The acid is then run off and a fresh quantity added and the stirring repeated. This operation is carried on, until the oil, washed with water, only imparts a pale yellow colour to the acid. The oil is then washed with water, dried over calcium chloride, and distilled over sodium. The distillate 174–175° is collected, and is practically pure cymene. Its conversion into thymol will be dealt with later (see "thymol").

## Terpenes, $C_{10}H_{16}$

The terpenes are leading constituents of the majority of the essential oils of plants, in many of which they exist in greater or less proportion. Terpenes are also obtainable by the dehydration of certain of the oxygenated compounds of the composition $C_{10}H_{18}O$ contained in various natural essential oils, and by the reduction of some alcohols and ketones of the composition $C_{10}H_{16}O$.

The terpenes are all isomerides of the molecular formula $C_{10}H_{16}$. With the single exception of camphene (solid), they are colourless liquids, lighter than water, and usually volatile without decomposition. They distil unchanged in a vacuum or a current of steam. The terpenes present a close similarity in their physical properties, a fact which renders their isolation and differentiation extremely difficult. This difficulty is further increased by the tendency which the terpenes exhibit, as a class, to pass from one into the

other under very slight provocation, and by the ability of some of them to exist in several different modifications, *e. g.*, dextrorotatory and lævorotatory and as mixtures of these which, when in equal proportions, give rise to inactive or racemic products.   As a result, the earlier investigators seldom obtained exactly the same product from two different botanical sources, and this circumstance led to the supposed discovery of innumerable terpenes, which were generally named by adding the suffix *ene* to one of the botanical names of the plant from which the oil had been obtained.   Personal equation in the details of the method of preparation, further led to different descriptions being given to the product from the same plant.

A marked advance in the knowledge of terpenes and their allies was made by Berthelot, who observed that the terpene of American turpentine oil rotated the plane polarisation of light to the right, while the terpene of French turpentine oil was lævorotatory.   Tilden and Shenstone further distinguished between the terpenes of the *pinene* group, $C_{10}H_{16}$, boiling at 156° to 160°, constituting the chief constituents of the essential oil of the *Coniferæ* and *Labiatæ*, and the "citrenes" (now called limonenes), boiling at about 175°, constituting the greater part of the oils from the *Aurantiaceæ* and *Umbelliferæ*.   In the meantime, the crystalline additive compounds formed by the terpenes with hydrochloric acid had been studied, and Tilden and his collaborators had discovered the interesting compounds of the terpenes with nitrosyl chloride (NOCl) and nitrogen trioxide.   At this point, O. Wallach commenced the remarkable researches which, in conjunction with those of Brass, Conrady, Bruhl, Baeyer, Otto and Gildemeister, and others, have, since 1884, placed the knowledge of the terpenes and their allies in a new light, and rescued their chemistry from the previous confusion.   These remarkable results were for the most part obtained by the study of the action, on the terpenes and their allies, of water, of the halogens and their hydrogen compounds, of oxidising agents, of nitrous acid and nitrosyl chloride, and of the compounds which the products of the action of the last two reagents formed with bases.

The more modern work of W. H. Perkin, Jr., and his pupils has, however, done more, perhaps, than any other researches, towards definitely settling the constitution of several of the terpenes.

The formation of the *bromides* is best observed by dissolving 1 volume of the terpene in 4 volumes of alcohol and 4 of ether.   The

solution is well cooled by ice, and then 0.7 volume of bromine is slowly added. The crystalline precipitate is washed with cold alcohol and recrystallised from ether.

The *nitroso-chlorides* of the terpenes were originally obtained by W. A. Tilden by the action on the oils of nitrosyl chloride gas, whereby compounds of the formula $C_{10}H_{16}NOCl$ were obtained. A more convenient method is that of Wallach (*Annalen*, 1888, **245**, 241), who mixes 14 c.c. of the terpene (pinene, limonene, sylvestrene) with 20 c.c. of amyl nitrite and 34 c.c. of glacial acetic acid. This mixture is well cooled, and half its volume of a mixture of equal volumes of glacial acetic and fuming hydrochloric acids gradually added, allowing time for the blue coloration to disappear before adding more of the mixed acids. The *nitroso-bromides* may be obtained in a similar manner.

On treating the terpene nitroso-chlorides with alcoholic potassium hydroxide or cautiously heating them alone, the elements of hydrochloric acid may be removed and products of the composition $C_{10}H_{15}NO$ obtained.

By treating the terpenes with nitrogen trioxide, *terpene nitrosates* are formed, of the composition $C_{10}H_{16}NO(ONO_2)$. Wallach prepares such compounds by treating a well-cooled mixture of equal volumes of the terpene and amyl nitrite with 0.5 volume of glacial acetic acid and 1 voume of nitric acid of 1.4 sp. gr.

On warming the nitroso-chlorides of the terpenes with excess of piperidine, aniline, or benzylamine, in alcoholic solution, a series of bases are formed which are applicable to the differentiation of the terpenes.

The table on p. 430 gives the characters of the more important of the terpenes:

**Constitution of Terpenes.**—The constitutional formulæ of the terpenes have been the subject of much controversy and ingenious speculation. The drastic methods of the earlier investigators had the unfortunate result of bringing about profound intramolecular changes in the plastic materials of the terpenes and led to the formulation of many erroneous and contradictory conclusions. The use of acid reagents, in particular, was often responsible for unsuspected isomeric changes. Later workers, profiting by the experiences of their predecessors, have relied chiefly on gentle oxidation by alkaline permanganate solutions and on synthetical experiments.

GENERAL CHARACTERS OF TERPENES

| | Pinene | Camphene | Fenchene[2] | Limonene[3] | Dipentene or dl-limonene[3] | Sylvestrene[1] | Terpinolene | Thujene |
|---|---|---|---|---|---|---|---|---|
| Sp. gr. at 15° | 0.864 | 0.855 at 40° | 0.863 – 0.869 | 0.849 | 0.849 | 0.851 | 0.854 | 0.851 |
| Sp. rot. [α]D | +48.5° | ±104° | +10° to −32° | + and − 105° to 107° | 0° | +70° to +94° | 0° | |
| Ref. index [n]D at 20° | 1.4655 | | 1.4690 | 1.4750 | 1.4750 | 1.4757 | 1.4840 | 1.4760 |
| B. p.,° | 156° | 160° 51 to 52° m.p. | 151-158° | 176° | 176° | 176° to 180° | 185° | 172 to 175° |
| Monohydrochloride, $C_{10}H_{16}.HCl$, m. p. | saturated; crystalline, 127° | crystalline; 152°-155° | liquid | unsaturated; liquid | unsaturated; liquid | liquid | | |
| Dihydrochloride, $C_{10}H_{16}$, 2HCl, m. p. | | | | 50° | 50° | 72° | | |
| Dibromide, $C_{10}H_{16}Br_2$, m. p. | 169° | 90° | liquid | | | | 69° | |
| Tetrabromide, $C_{10}H_{16}Br_4$, m. p. | | | liquid | 104° | 125° to 126° | 135° | 116° | |
| Nitroso-chloride, $C_{10}H_{16}$, NOCl, m. p. | about 109° | no compound | | 100° to 104° | 103° to 104° | 107° | | |
| Nitroso-derivative: Formula, m. p. | $C_{10}H_{16}NO$ 132° | | | $C_{10}H_{16}N.OH$ 72° | $C_{10}H_{16}N.OH$ 93° | | | |
| Benzyl-nitrolamine, $C_{10}H_{16}(NO)NH.C_7H_7$, m. p. | 122° | | | 92° | 110° | 71° | | |
| Chief sources or modes of formation. | Turpentine and juniper oils (Coniferæ); sage oil (Labiatæ). | Isomerisation of pinene. Reduction of camphor and borneol. | Reduction of fenchone from fennel oil. | Oils of neroli, orange-peel, lemon, lime and bergamot (Aurantiaceæ); oils of dill and caraway (Umbelliferæ), etc. | Isomerisation of other terpenes; elemi, turpentine and other oils. | Russian and Swedish turpentine oils (Coniferæ). | Isomerisation of other terpenes. | Artificially from thujene, contained in thuja oil. |

[1] Several isomeric fenchenes exist.   [2] Including carvestrene, the optically inactive variety, except as to optical rotation.
[3] Two isomeric nitrosochlorides exist.

Most of the terpenes may be derived from the hydrocarbon *p-menthane*, $C_{10}H_{20}$, previously mentioned, having the constitution of a *methyl isopropyl cyclohexane*.[1]

$$CH_3.CH \big\langle \begin{matrix} CH_2-CH_2 \\ CH_2-CH_2 \end{matrix} \big\rangle CH.CH \big\langle \begin{matrix} CH_3 \\ CH_3 \end{matrix}$$
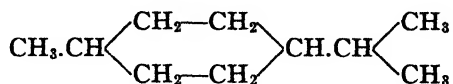
This compound is closely related to cymene, from which it may be derived by reducing the aromatic nucleus. Conversely it may be converted into cymene by oxidation.

The terpenes, $C_{10}H_{16}$, which are intermediate between cymene, $C_{10}H_{14}$, and *p*-menthane, $C_{10}H_{20}$, differ from the latter compound by 4 atoms of hydrogen in the molecule and must therefore contain, in addition to the hexamethylene ring,

I. Two double bonds, as in the **monocyclic terpenes;** or

II. A double bond and a second ring system, as in the **dicyclic terpenes;** or

III. Two additional ring systems, giving a total of 3 independent rings; no terpene of this type is definitely known.

It may be noted that while the 3 double bonds of cymene[2] are all in the nucleus, the double bonds of the terpenes may be either in the central ring system, or in the side chains. In the latter case there is a marked tendency for the double bonds to migrate into the nucleus.

### Monocyclic Terpenes

The following formulæ have been established fairly definitely by synthetic and other methods:

I. **Limonene** (dipentene) and

II. **Terpenolene** derived from terpineol[3] by removal of a molecule of water by means of potassium hydrogen sulphate and alcoholic sulphuric acid, respectively.

III. **β-Phellandrene,** synthesised by Kondakow and Schindelmeiser (*J. pr. Ch.*, 1905, [2], **72,** 193; 1908, **75,** 141). These 3 terpenes contain 1 double bond in the nucleus and 1 in a side chain; the 2 following contain 2 double bonds in the nucleus and may therefore be described correctly as dihydro-p-cymenes.

[1] The formula shows the constitution of the *p*-compound; a few of the terpenes (see Carvestrene and Sylvestrene) are derived from the *m*-isomeride.
[2] Using for convenience the Kekulé formula for benzene.
[3] Synthesised by Perkin (Trans. 1904. **85,** 654).

IV. **α-Terpinene,** produced by means of sulphuric acid from the preceding terpenes by isomeric changes involving the transfer of a double bond from the side chain to the nucleus.

V. **α-Phellandrene.**   Synthesised by Harries and Johnson (*Ber.*, 1905, **38**, 1832).

Somewhat separated from the above terpenes is

VI. **Sylvestrene,** the *m*-compound analogous with dipentene.

The monocyclic terpenes are for the most part characterised by the formation of tetrabromides, while the dicyclic terpenes usually form only dibromides, though they often add on 2HBr, owing to the rupture of one of the ring systems by the acid.

## MONOCYCLIC TERPENES.
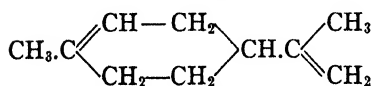
$$CH_3.C\underset{CH_2-CH_2}{\overset{CH-CH_2}{\diagup\diagdown}}CH.C\underset{CH_2}{\overset{CH_3}{\diagup}}$$
Limonene (dipentene).

$$CH_3.C\underset{CH_2-CH_2}{\overset{CH-CH}{\diagup\diagdown}}C.CH\underset{CH_3}{\overset{CH_3}{\diagup}}$$
Terpinene.

$$CH_3.C\underset{CH^2-CH_2}{\overset{CH-CH_2}{\diagup\diagdown}}C=C\underset{CH_3}{\overset{CH_3}{\diagup}}$$
Terpinolene.

$$CH_2=C\underset{CH=CH}{\overset{CH_2-CH_2}{\diagup\diagdown}}CH.CH\underset{CH_3}{\overset{CH_3}{\diagup}}$$
β-Phellandrene.

$$CH_3.C\underset{CH=CH}{\overset{CH-CH^2}{\diagup\diagdown}}CH.CH\underset{CH_3}{\overset{CH_3}{\diagup}}$$
α-Phellandrene.
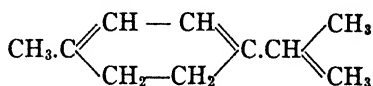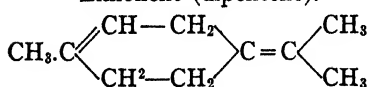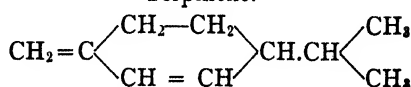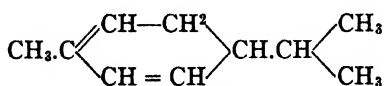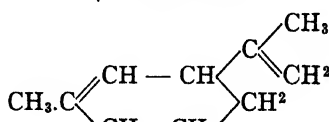
$$CH_3.C\underset{CH_2-CH_2}{\overset{CH-CH}{\diagup\diagdown}}\overset{C\underset{CH^2}{\overset{CH_3}{\diagup}}}{CH^2}$$
Carvestrene (sylvestrene).

## Limonene, $C_{10}H_{16}$

**Limonene** is a very frequent constituent of essential oils, and some of the oils from the *Aurantiaceæ* are almost wholly composed of it. Besides occurring largely in these oils, limonene exists largely in the oils of some of the *Umbelliferæ*.   Thus it forms about 60% of oil of dill, and is not much less abundant in oil of caraway, being in each case associated with carvone.   The oil from *Erigeron canadense* is stated to consist almost entirely of limonene, which also occurs in appreciable quantity in some pine oils, in massoya oil (from the bark of *Cinnamomum kiamis*), and in the oil from jaborandi leaves.

The terpenes known as *citrene, bergamene, hesperidene, carvene*, etc., are merely limonene containing traces of impurities varying with the

|  | Terpinene-α | Terpinene-β | Terpinene-γ | Phellandrene-γ | Phellandrene-β | Sabinene |
|---|---|---|---|---|---|---|
| Sp. gr. at 15°. | 0.844 | 0.845 | 0.848 | 0.847–0.848 | 0.8485 | 0.846 |
| Sp. rot. [α]D. | | | +0°.32 | +40° (*dextro*) −8.4° (*laevo*) | +18° (*dextro*) ? (*laevo*) | +66° |
| Ref. index [α]D at 20°. | 1.4800 | 1.4800 | 1.4765 | 1.4730 to 1.4760 | 1.4788 | 1.4675 |
| B. P. | 180° at 735 mm. | 62° at 10 mm. | 177°–178° | 174–175° | | 162°–166°. |
| Monohydrochloride $C_{10}H_{16}.HCl$ | | | | | | |
| m. p. | | | | | | |
| Dihydrochloride $C_{10}H_{16}.2HCl$ | 52°(?) | 52°(?) | 52°(?) | | | Yields terpinene dihydrochloride. |
| m. p. | | | | | | |
| Dibromide $C_{10}H_{16}.Br_2$ m. p. | | | | | | |
| Tetrabromide $C_{10}H_{16}.Br_4$ m. p. | | | | | | |
| Nitroso-chloride $C_{10}H_{16}.NOCl$ | | | | | | |
| m. p. | | | | | | |
| Nitroso derivative formula m. p. | 155° $C_{10}H_{16}N_2O_2$ | | | 112°[1] 105°[2] $C_{10}H_{16}N_2O_3$ | 102°[1]; 98°[2] $C_{10}H_{16}N_2O_3$ | |
| Benzyl-nitrolamine. | | | | | | |
| Chief sources or modes of formation. | Coriander and other oils. | Isomerisation of carvenene. | Coriander and other oils. | Bitter fennel and elemi oils. | Water fennel oil | Savin and other essential oils. |

[1] α-nitrite.   [2] β-nitrite.

origin of the oils from which they are prepared. To these very persistent impurities the characteristic odours of apparently different substances are frequently due.

The limonene in the oils from the *Aurantiaceæ* and caraway oil is chiefly dextrorotatory ($[a]_D = +106.8°$), and the large proportion in which it is present imparts this character to these oils; but the limonene of the oils distilled from the leaves of *Pinus sylvestris* is lævorotatory to an almost equal extent ($[a] = -105°$). The oils of lemon, lime, and caraway contain a mixture of the 2 limonenes. By mixing equal parts of dextro- and lævo-limonene, an optically inactive terpene is obtained, which is identical with dipentene.

Limonene is liquid of pleasant odour, boiling at 175° to 176°, and having a sp. gr. of 0.849 at 20°. Hence it is lighter and has a higher b. p. than pinene.

**Inactive limonene or dipentene** obviously is present in essential oils where limonene of low optical rotation is found; this lemon oil contains dipentene with excess of *dextro*-limonene. It is stated to form a considerable proportion of elemi oil, in which it exists with phellandrene and traces of polyterpenes and oxygenated compounds. Wallach also found it in considerable quantity in the essential oil of the camphor-tree, and according to Brühl, it also occurs in oil of cascrilla. The oils of bay, turpentine, cardamoms, massoya, mace, bergamot, fennel, and myrtle are stated to contain more or less dipentene; but in view of the facility with which certain other terpenes (especially pinene) are converted into dipentene by the action of heat, acids, etc., the presence of this terpene in essential oils which have been exposed to slightly abnormal conditions is only to be expected. It seems highly probable that the loss in optical activity observed in some oils by storing or heating is frequently due to the formation of inactive dipentene from various optically active terpenes. The inactive terpene is conveniently prepared from the dihydrochloride by boiling with 1 part of sodium acetate and 2 parts of glacial acetic acid for half an hour in a flask furnished with a reflux condenser. The product which was originally called terpilene is then distilled with steam, the oil which distils boiled with potassium hydroxide, redistilled, dried, and purified by fractional distillation. It has recently been synthesised by W. H. Perkin, Jr., starting from pentane tri-carboxylic acid (Trans., 1904, **85**, 654);

the synthetic product differs from active limonene only in being optically inactive.

**Active limonene hydrochloride,** $C_{10}H_{16}HCl$, prepared by passing a stream of dry hydrochloric acid gas through dry limonene, is a liquid, b. p. 97° to 98° under 11–12 mm. pressure, sp. gr. 0.982, and $[\alpha]_D \pm 40°$.

**The dihydrochloride,** $C_{10}H_{16}$, 2HCl, usually known as dipentene dihydrochloride, is produced in an inactive form by the action of moist hydrogen chloride on active limonene, inactive dipentene, or active pinene. It may be prepared conveniently by mixing a solution of dipentene or limonene in glacial acetic acid, with glacial acetic acid saturated with hydrogen chloride gas. The dihydrochloride crystallises from a mixture of alcohol and ether in rhombic plates, having a peculiar odour and melting at 50°. It boils at 118° to 120° at 10 mm. pressure. By the method described above, dipentene can be reproduced from the dihydrochloride; but more or less *terpinene* and *terpinolene*, besides *cymene* and small quantities of a *paraffinoid hydrocarbon*, appear to be constant secondary products (Tilden and Williamson, Trans. 1893, **63**, 292).

The dihydrochloride is decomposed by boiling with water or alcoholic potassium hydroxide with formation of *terpineol*, $C_{10}H_{17}.OH$.

When the dihydrochloride is treated with a drop of a concentrated solution of ferric chloride and the mixture gently heated, a rose coloration is produced, which changes to an intense violet-red, and ultimately to blue. To obtain the reaction, which was first observed by Riban (*Ann. Chim. Phys.*, [5], **6**, 37), it is not necessary to prepare the hydrochloride previously, but a few drops of lemon, turpentine, or other oil containing a terpene which yields dipentene dihydrochloride on treatment with moist hydrogen chloride (*e. g.*, pinene, limonene) may be stirred in a porcelain capsule with a drop of concentrated hydrochloric acid, and a drop of a strong solution of ferric chloride. As the sesquiterpenes do not form dihydrochlorides, the test may be used to detect pinene and other terpenes in presence of the former compounds.

**Dipentene dihydrobromide,** $C_{10}H_{16}$,2HBr, is obtained by saturating glacial acetic acid with hydrogen bromide gas, and adding a solution of limonene or dipentene in glacial acetic acid. The compound separates at once in crystals, m. p. 64°, and closely resembles the dihydrochloride.

According to Baeyer, the dihydrochloride and dihydrobromide of cinene each exists in 2 isomeric forms, comparable to maleic and fumaric acids. The usually occurring or *trans*-modification of the dihydrochloride melts at 50°, whereas the *cis*-form prepared from cineol and hydrochloric acid, melts at 25°. Similarly the *trans*-modification of the dihydrobromide melts at 64°, while the *cis*-form, prepared from cineol, melts at 39°. Both forms easily regenerate dipentene.

**Active limonene tetrabromide,** $C_{10}H_{16}Br_4$, is obtained by acting with bromine on limonene dissolved in 10 parts of glacial acetic acid. It separates in hemihedral rhombic crystals, which are soft and pliable, and when recrystallised from ethyl acetate melts at 104°.

**The inactive (dipentene) tetrabromide,** m. p. 124°, prepared from inactive dipentene or by mixing the *d*- and *l*-tetrabromides, is less readily soluble in ether.

**Limonene nitrosochloride,** $C_{10}H_{16}NOCl$, prepared by passing nitrosyl chloride into a solution of limonene or oil of orange-peel in 5 parts of methylated spirit, cooled to − 10°, or by Wallach's method, described on page 429, separates in crystals, m. p. 103°. By boiling with alcoholic potassium hydroxide it is converted into *carvoxime*, $C_{10}H_{14}(N.OH)$, by elimination of a molecule of hydrogen chloride; the identity of the two products—nitroso-limonene and carvoxime—is of considerable value in deducing structural formula for limonene and for carvone.

The nitrosochloride, prepared from either dextro- or lævo-limonene, is always a mixture of two distinct isomerides ($\alpha$ and $\beta$), one of which is more powerfully rotatory than the other; a separation can be effected by treating the mixture with cold ether or chloroform. In addition to the above 4 optically active nitrosochlorides, inactive modifications may be prepared by mixing equal weights of the *d*- and *l*-forms of the $\alpha$- and $\beta$-nitrosochlorides.

By warming limonene nitrosochlorides in alcoholic solution with piperidine, aniline, benzylamine, etc., Wallach obtained a series of crystalline $\alpha$- and $\beta$-notrolamines the rotation and m. p. of which are shown in the table on page 437.

The various nitrolamines from dextro- and lævo-limonene unite to form inactive compounds, in a manner similar to the nitrosochlorides from the same sources. Thus, when equal quantities of the $\alpha$-dextro- and lævo-nitrolpiperidines, m. p. 94°, are dissolved in petroleum

## CHARACTERS OF LIMONENE AND DERIVATIVES

| Compound | Formula | Source | | | | |
|---|---|---|---|---|---|---|
| | | Dextro-limonene | | Lævo-limonene | | Dipentene |
| | | Sp. rot., ° [α]D | M. p. | Sp. rot., ° [α]D | M. p. | M. p. |
| Terpene | $C_{10}H_{16}$ | $+125°$ | ...... | $-125°$ | ...... | ...... |
| Monohydrochloride | $C_{10}H_{16}.HCl$ | $-40.0$ | ...... | $+39.5$ | ...... | ...... |
| Tetrabromide | $C_{10}H_{16}Br_4$ | $-73.27$ | $104°$ | $-73.45$ | $104°$ | $124°$ |
| α-nitrosochloride | $C_{10}H_{16}NOCl$ | $+313.4$ | $103-104°$ | $-314.8$ | $103-104°$ | $103-104°$ |
| β-nitrosochloride | $C_{10}H_{16}NOCl$ | $+240.3$ | $100°$ | $-242.2$ | $100°$ | $154°$ |
| α-nitrolpiperidine | $C_{10}H_{16}NO.N(C_5H_{10})$ | $+67.75$ | $94°$ | $-67.60$ | $94°$ | $152°$ |
| β-nitrolpiperidine | $C_{10}H_{16}NO.N(C_5H_{10})$ | $-60.48$ | $111°$ | $+60.18$ | $110°$ | $125°$ |
| α-nitrolaniline | $C_{10}H_{16}NO.NHPh.$ | ...... | $112°$ | ...... | $112°$ | $149°$ |
| β-nitrolaniline | $C_{10}H_{16}NO.NHPh.$ | ...... | $153°$ | ...... | $153°$ | $149°$ |
| α-nitrolbenzylamine | $C_{10}H_{16}.NO.NH(C_7H_7)$ | $+163.8$ | $92°$ | $-163.6$ | $92°$ | $110°$ |
| α-nitrolbenzylamine hydrochloride | $C_{10}H_{16}NO.NH(C_7H_7)HCl$ | $-82.26$ | ...... | $+83.06$ | ...... | ...... |
| Carvoxime | $C_{10}H_{14}.NOH.$ | $-39.34$ | $72°$ | $+39.71$ | $72°$ | $93°$ |
| Benzoyl-carvoxime | $C_{10}H_{14}.NOBz.$ | $-26.97$ | ...... | $+26.47$ | ...... | ...... |

spirit and the solutions mixed, a sparingly soluble inactive nitrol-
piperidine, m. p. 154°, is at once precipitated.   A similar inactive
compound, m. p. 152°, is obtained by mixing the solutions of the
β-nitrolpiperidines.

It will be noticed that the racemic compounds differ very widely
from the optically active isomerides from which they are prepared; it
is therefore not surprising that the identity of racemic or *dl*-limonene
with dipentene remained for a long time unrecognised.

## Terpinolene

Terpinolene is rarely met with in nature.    It is, however, produced
regularly by the isomerisation of other terpenes, and by the dehydra-
tion of such alcohols as terpineol and linalol.    It has been found in
the essential oil of Manila elemi.    Its probable constitution is

$$C—CH_3$$
$$H_2C \quad CH$$
$$H_2C \quad CH_2$$
$$C:C(CH_3)_2$$
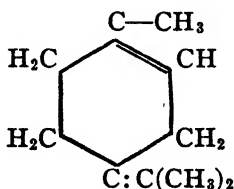
It was originally discovered by Wallach (*Annalen*, **227**, 283) as the
result of heating oil of turpentine with alcoholic sulphuric acid.
It is also obtained by the dehydration of terpineol by oxalic acid, and
constitutes a large proportion of the waste products in terpineol
manufacture.    It can be obtained in a pure condition by converting
the crude product into its tetrabromide, and reducing this with
zinc dust and alcohol.

So prepared, pure terpinolene has the following characters:

Sp. gr. at 15.5°..................................... 0.854
Ref. index at 20°.................................... 1.4840
B. p. .............................................. 183°
Opt. rot. .......................................... 0°

The tetrabromide is the most characteristic compound for the
identification of terpinolene.    It is prepared by adding gradually
four atoms of bromine to a solution of the terpene in glacial acetic
acid, at a low temperature.    It melts at 116–117°.

## Terpinene

The terpene known as terpinene until recently is undoubtedly a mixture of several compounds, and the chemistry of these substances is still in an unsettled condition. There are at least three hydrocarbons known under this name, which are now discribed as $\alpha$-terpinene, $\beta$-terpinene and $\gamma$-terpinene. These substances have the following constitutions:



$\alpha$-Terpinene     $\beta$-Terpinene     $\gamma$-Terpinene
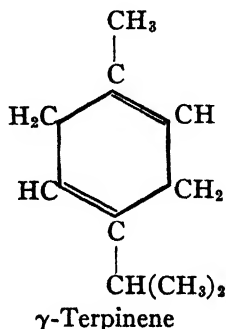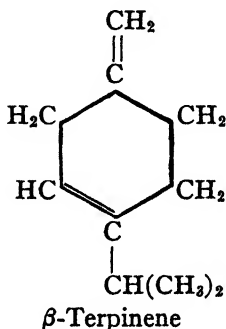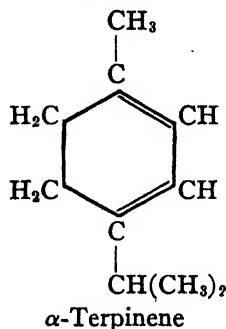
Only $\alpha$-terpinene and $\gamma$-terpinene have been found occurring naturally in essential oils, but all three can be obtained artificially from other terpenes or their alcohols.

$\alpha$-terpinene, which occurs in Cardamom oil, has the following approximate characters:

Specific gravity at 15.5°.............................. 0.846
Boiling point........................................ 178°
Refractive index at 20°.............................. 1.4790

$\gamma$-terpinene, obtained from Coriander oil, and possibly containing a little $\alpha$-terpinene, has the following characters:

Sp. gr. at 15.5°.................................... 0.8485
B. p............................................... 177–178°
Opt. rot........................................... +0° 32'
Ref. index at 20°.................................. 1.4765

Owing to the somewhat indefinite character of this terpene, methods of identification are somewhat uncertain. The most characteristic compound for identifying $\alpha$-terpinene is the nitroso compound, $C_{10}H_{16}N_2O_3$, which melts at 155°. If 2–3 grm. are dissolved in an equal volume of petroleum spirit, and mixed with an equal volume of water containing 2–3 grm. of sodium nitrite, and glacial acetic acid is added with continual stirring (the tem-

perature being kept to 0°) crystals of terpinene nitrosite separate out, which can be recrystallised from hot alcohol.   γ-Terpinene is recognised by yielding, on oxidation with potassium permanganate, erythritol, melting at 236°–237°.   To obtain this product, 140 grm. of the substance are shaken with 280 grm. of potassium hydroxide and 660 grm. of potassium permanganate, 8 litres of water and 8 kilos of ice.   The resulting crystals are recrystallised from 25% alcohol and will be found to melt at 236°–237°.

## Phellandrene,  $C_{10}H_{16}$

Until recently, phellandrene was thought to exist only in optically isomeric (dextro and lævo) modifications.   Recently, however, the existence of structural isomerides, known as α- and β-phellandrene, has been recognised and to these the structural formulæ shown on p. 432 have been assigned (Semmler, *Ber.*, 1903, **36**, 1749; Wallach, *Ann.*, 1904, **336**, 9; 1905, **304**, 1).   α-*Phellandrene* exists in a dextro-rotatory form, the optical rotation being +40°40′, in the oils of elemi and bitter fennel, and in a lævorotatory form in eucalyptus oil. It boils at 61° under 11 mm. pressure, has sp. gr. 0.844 at 19°, $n_D$ 1.4732.   Phellandrene is one of the most easily altered of the terpenes.   It is radically changed by contact with acids, and is largely converted into terpinene by the action of hot alcoholic sulphuric acid.

The compounds of phellandrene with the halogens and halogen acids are not very characteristic.   The *bromide* is a heavy oil which is converted into dipentene by heating with acetic acid and sodium acetate.

The most characteristic derivative is the *nitrosite*, $C_{10}H_{16}(NO)NO_2$, prepared by agitating the hydrocarbon with sodium nitrite and acetic acid.   Wallach describes the following process for its preparation: Phellandrene is diluted with petroleum spirit and treated with dilute sulphuric acid in a beaker surrounded with a freezing mixture.   A solution of sodium nitrite is then run in gradually, care being taken not to allow the temperature to rise above 4°.

Two modifications are produced, which may be separated by recrystallising from acetone and alcohol: α-*phellandrene* α-*nitrosite*, m. p. 112° to 113°, has $[\alpha]_D \pm 138°$; α-*phellandrene* β-*nitrosite*, m. p. 105°, has $[\alpha]^D \pm 40$ to 46°; they have similar chemical properties and are perhaps stereoisomers.

*β-Phellandrene*, b. p. 57° under 11 mm. pressure, has sp. gr. 0.8520, $n_D$ 1.4788 at 20°, and optical activity from +15° to +18° 30'; only the dextrorotatory form is known as a constituent of water-fennel oil. *β-Phellandrene α-nitrosite*, m. p. 102° has $[\alpha]_D$ − 159.30°; *β-phellandrene β-nitrosite*, m. p. 97° to 98°, is optically inactive.

## Sylvestrene, $C_{10}H_{16}$

Sylvestrene occurs in Swedish and Russian turpentine oils together with dextro-pinene and hydrocarbons of higher b. p.[1] It is a liquid having an odour like that of fresh pine-wood.

Sylvestrene is one of the most stable of the terpenes, retaining its optical activity at 250° and undergoing little change by the action of alcoholic sulphuric acid. It combines with 2 molecules of hydrogen chloride, bromide and iodide, yielding compounds which melt, respectively, at 72°, 72° and 66°. From the crystalline dihydrochloride, sylvestrene may be recovered unchanged by boiling with aniline. *Sylvestrene tetrabromide* forms monoclinic tablets, m. p. 135°. The *nitrosochloride* is very soluble in chloroform, and strongly dextrorotatory.

A fine blue coloration is produced on adding a drop of strong sulphuric acid to a solution of sylvestrene in acetic anhydride; this property is not shared by any other terpene.

The inactive racemic form of sylvestrene was first prepared by Baeyer (*Ber.*, 1894, **27**, 1915, 3485; 1896, **29**, 2796) and was described by the name "*carvestrene.*" It has since been synthesized by W. H. Perkin, Jr. (*J. Chem. Soc.*, 1908, **93**, 1876).

## Dicyclic Terpenes

### Pinene, $C_{10}H_{16}$

Although there are four well recognised terpenes known as α-pinene, β-pinene, δ-pinene and isopinene, the only one of commercial importance is α-pinene, which occurs in numerous essential oils and is the principal constituent of most turpentine oils. Apart from its use in the form of turpentine, it is of commercial importance as the crude material for the manufacture of artificial camphor It is the most commonly occurring of all the constituents of essential oils. It is optically active and is found freely in

---

[1] Swedish turpentine oil is obtained from the *tar* resulting from the dry distillation of the roots and stumps of pines, whereas American turpentine oil is made from the resinous exudation of the same species of pine. This difference in origin may account for the absence of sylvestrene from the American oil.

both the dextrorotatory and the laevorotatory forms. It can be obtained in the dextrorotatory form from American or Greek oil of turpentine, and from the French oil as laevo-pinene. The purest specimens obtained have the following characters:

|  | DEXTRO-α-PINENE | LAEVO-α-PINENE |
|---|---|---|
| B. p.................................. | 155°–156° | 155°–156° |
| Sp. gr. at 15.5°...................... | 0.864 | 0.865 |
| Sp. rot.............................. | +48.4° | −48.6° |

It can be obtained in the optically inactive forms by heating the nitrosochloride with aniline.

A number of well defined crystalline compounds of this and most other terpenes are known, and are useful for identification purposes. Of these the nitrosochloride is one of easiest to prepare. Pinene is dissolved in three times its volume of petroleum spirit, cooled to 0°, and an 8% solution of nitrosyl chloride in equal volumes of petroleum spirit and chloroform added slowly with constant stirring. Alcohol is then added and the crystalline precipitate washed with alcohol and dried at 50°. The melting point is not known with certainty, as, although it usually melts when prepared as above, at 103°, its melting point can be raised to 115° by repeated recrystallisation from chloroform. Its formula is $(C_{10}H_{16}.NOCl)_2$.

Pinene hydrochloride $C_{10}H_{16}.HCl$ is another easily prepared crystalline substance useful for identification purposes. This substance somewhat resembles camphor in appearance and odour, and was originally termed "artificial camphor," but must not be compared with true artificial camphor. Pinene hydrochloride is obtained by passing a current of absolutely dry hydrochloric acid gas into absolutely dry pinene, the temperature being kept low all the time. The crystalline mass is pressed between porous paper and recrystallised from alcohol-ether. It then melts at 127°. The reaction causes an intra-molecular change, so that on withdrawing HCl, pinene is not regenerated, but camphene results. Pinene hydrochloride is identical with isobornyl chloride. α-Pinene has the following constitution:
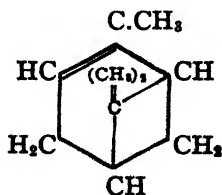
Pinene forms an important hydration product, terpin hydrate. If the terpene be allowed to remain in contact with a dilute mineral acid for some time, at room temperature, terpin hydrate $C_{10}H_{18}(OH)_2 + H_2O$ results.

A mixture of 8 parts of pinene, 2 parts of alcohol, and 2 parts of nitric acid (sp. gr. 1.250) is placed in a flat evaporating basin. After standing for several days, the liquid is decanted from the crystalline mass formed, and neutralised with alkali, when a second crop of crystals is obtained. Terpin hydrate melts at 116–117° and when dried over sulphuric acid, yields terpin $C_{10}H_{18}(OH)_2$ melting at 104–105°. Terpin has the constitution

$$COH.CH_3$$

$$H_2C \quad CH_2$$

$$H_2C \quad CH_2$$

$$COH.CH.(CH_3)_2$$
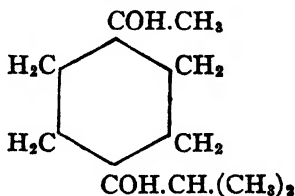
### Camphene, $C_{10}H_{16}$

Camphene is found only rarely in nature, but it is of importance from its relation to pinene, borneol, and camphor. It occurs among the products of the action of concentrated sulphuric acid on turpentine oil, and is an important constituent of the so-called "terebene."

Pure camphene may be prepared from pinene hydrochloride by heating it with potassium stearate or dry soap to 200° or 220°. It is also readily obtained by heating equal weights of the hydrochloride and anhydrous sodium acetate to 200° for several hours, with twice their weight of glacial acetic acid; or by simply boiling a mixture of pinene hydrobromide and glacial acetic acid under a reflux condenser.

Camphene may also be prepared by warming bornyl chloride, $C_{10}H_{17}Cl$, with an equal weight of aniline, and then heating the mixture to about 180°. The formation of aniline hydrochloride occurs suddenly, and the action is complete in a few minutes. When cold, the product is treated with hydrochloric acid, and the camphene distilled off in a current of steam. Camphene is also produced when *bornylamine*, $C_{10}H_{17}NH_2$ is heated with acetic anhydride. Ammonia is split off in the action, leaving camphene.

Camphene is the only well recognised solid terpene found natu-
rally.   It is a crystalline substance having the following characters:

M. p.......................................... 50°–52°
B. p.......................................... 159°–161°
Sp. rot........................................ about ±104°
Rep. index at 20°............................. 1.4550 at 50°
Sp. gr. at 15.5°............................... 0.8555 at 40°

Camphene is identified in the following manner.   One hundred
grams of the fraction containing camphene in appreciable quantity
are mixed with 250 grm. of glacial acetic acid and 10 grm. of 50%
sulphuric acid.   The mixture is heated for two to three hours on a
water bath to 60°, and after the reaction is complete, excess of water
is added and the separated oil is repeatedly washed with water.   It
is then saponified by alcoholic potash solution, the reaction mass
heated to evaporate water and the residue recrystallised from petro-
leum spirit.   The isoborneol so obtained melts (in a sealed tube)
at 212°, or, as is usually the case, at 203°–205° unless carefully
purified.   Camphene has the constitution

$$C:CH_2$$
$$HC \overbrace{\phantom{xxxxxx}} C(CH_3)_2$$
$$CH_2$$
$$H_2C \underbrace{\phantom{xxxxxx}} CH$$
$$CH_2$$
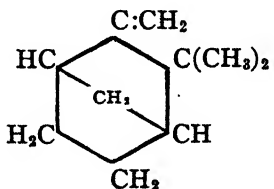
When prepared from pinene hydrochloride or hydrobromide, the
camphene obtained exhibits an optical rotation of the same kind as
that of the original pinene, but the product from bornyl chloride is
optically inactive.

Camphene readily unites with hydrochloric acid to form a cam-
phoroid substance, m. p. 157°, which is probably identical with *bornyl
chloride*.   The product differs from pinene hydrochloride by disso-
ciating into camphene and hydrochloric acid by distillation, or more
gradually by mere contact with water.

In contact with bromine, camphene is gradually converted into the
substitution-product $C_{10}H_{15}Br$.   It is generally stated not to form
an addition-product with bromine, but, according to Reychler, a *cam-
phene dibromide* can be obtained in prisms exhibiting double refrac-
tion and melting at 90°.

By treatment with oxidising agents, such as chromic acid mixture, camphene is converted into *camphor*, $C_{10}H_{16}O$, which exhibits an optical activity of the same kind as that of the camphene from which it was derived.

## Bornylene, $C_{10}H_{16}$

A terpene very closely related to camphene was obtained in admixture with camphene, when bornyl iodide was heated to 170° in an autoclave with strong alcoholic potassium hydroxide. The bornylene thus produced melts at 98°; and boils at 150° (Wagner and Brykner, *Ber.*, 1900, **33**, 2121). Bornylene and camphene are the only terpenes which are solid at ordinary temperatures.

## Fenchene, $C_{10}H_{16}$

Fenchene is a terpene which does not occur naturally, or if so, only to a very minute extent. There are several isomers known under the name fenchene, and it is doubtful whether any one of them has been isolated in an absolutely pure condition.

The substance usually known as fenchene may be prepared by reducing the ketone, fenchone, $C_{10}H_{16}O$ to its alcohol fenchyl alcohol $C_{10}H_{17}OH$, and splitting off water by the action of potassium bisulphate at a high temperature. Fenchene so prepared has the following characters:

```
Sp. gr. at 15.5°.................................. 0.867
B. p.............................................. 155-156°
Ref. index at 20°................................. 1.4690
```

Wallach (*Ann.*, **302**, 371; **315**, 273) found that when *d*-fenchone was reduced it yielded *l*-fenchyl alcohol which, by treatment with $PCl_5$ yielded two fenchyl chlorides, each of which gave a different fenchene. Wallach termed them *D-dextro*-fenchene and *D-lævo*-fenchene. Two corresponding fenchenes are obtained from *lævo*-fenchone, which Wallach termed *L-dextro*-fenchene and *L-lævo*-fenchene.

Komppa and Roschier (*Chem. Zeit.*, 1917, **1**, 407) propose to revise this complex nomenclature, and call Wallach's *D*-fenchene α-fenchene, and the terpene obtained by dehydrating fenchyl alcohol, β-fenchene.

It is probable that α-fenchene is identical with isopinene. These two substances thus designated have the following characters:

|  | α-FENCHENE | β-FENCHENE |
|---|---|---|
| Sp. gr. | o.866 at $\frac{20°}{4°}$ | o.866 at 15° |
| B. p. | 154–156° | 151–153° |
| Sp. rot. | ±32° (?) | +10.7° |

The constitution of α-fenchene (isopinene) is as follows:

$$
\begin{array}{c}
CH \\
H_2C \quad \overline{\qquad} \quad CH \\
C(CH_3)_2 \\
H_2C \quad \overline{\qquad} \quad C.CH_3 \\
CH
\end{array}
$$
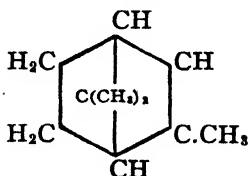
### Thujene, $C_{10}H_{16}$

Thujene has not yet been found occurring naturally, and several terpenes have been described under the name. The substance originally known as thujene was obtained by the distillation of thujylamine and is identical with Semmler's tanacetene. This substance has the following characters:

| | |
|---|---|
| Sp. gr. at 15.5°. | o.8508 |
| B. p. | 151–152° |
| Ref. index at 20°. | 1.4760 |

The following bodies have been described as thujene:

| NAME | B. P. | OPT. ROT. | REF. INDEX AT 20° |
|---|---|---|---|
| Semmler's Thujene.... | 60–63° at 14 mm. | ............. | 1.4760 |
| Wallach's Thujene.... | 170–172° | ............. | 1.4714 |
| Tschugaeff's Thujene.. | 151–153° at 670 mm. | ............. | 1.504 |
| Kondakoff's Thujene.. | o.825 to o.828 | +3° to +48° | about 1.4500 |

The most recent work on the subject is that of Kondakow and Skworzow (*Chem. Zentral*, 1910, **2**, 467), and they are of the opinion that every thujene hitherto described is a mixture and not a pure hydrocarbon substance. The chemistry of the subject requires elucidation. The probable formula for thujene is:

$$
\begin{array}{c}
C.CH_3 \\
HC \quad \overline{\qquad} \quad CH \\
H_2C \quad \overline{\qquad} \quad CH_2 \\
C(CH)(CH_3)_2
\end{array}
$$
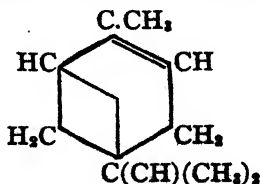
Isothujene, regenerated from its dihydrochloride possesses the following characters:

B. p............................................... 176–180°
Sp. gr. at 18°..................................... 0.854
Sp. rot............................................ +3.1°
Ref. index at 20°.................................. 1.4758

Thujene yields a characteristic colour reaction. If one drop of 50% sulphuric acid be added to a 5% solution in acetic anhydride a deep red colour results. This, however, must not be confused with the violet-red colour yielded by the sesquiterpene of gurjun balsam oil.

## Carene $C_{10}H_{16}$

Simonsen has recently (*J. Chem. Soc.*, 1920, 570; 1923, 549) isolated a terpene from the Indian turpentine oil from *Pinus longifolia*, and a very similar terpene from the oil of *Andropogon iwarancusa*. The characters of the terpene from Indian turpentine, which has been named carene, are as follows:

Sp. gr. $\frac{30°}{30°}$................................. 0.8586
Ref. index at 30° ................................ 1.4690
Opt. rot. ........................................ +7.7°
B. p............................................... 123–124°

With hydrogen chloride it yields a mixture of dipentene and sylvestrene hydrochloride. It yields a nitrosite, $C_{10}H_{16}N_2O_3$ melting at 141.5°. Its constitution is that of $d$-$\Delta^3$-Carene whilst that of the terpene from the andropogon oil is that of $d$-$\Delta^4$-Carene, as follows:



Δ³-Carene      Δ⁴-Carene
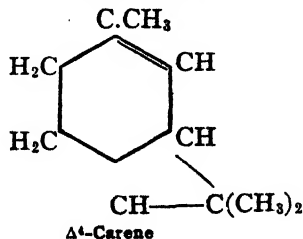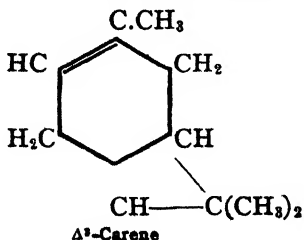
## Olefinic Terpenes, $C_{10}H_{16}$

There are two hydrocarbons of the formula $C_{10}H_{16}$ which are found in essential oils, and which have usually been grouped with the terpenes on account of their formulæ. These are myrcene and ocimene.

Myrcene is found in West Indian lemon-grass oil and in oil of Bay etc. It is an open chain compound and has one of the following constitutions:

$$(CH_3)_2C : CH.CH_2.CH_2.C(CH_2).CH : CH_2$$

or      $$(CH_3)(CH_2)C.CH_2.CH_2.CH_2.C(CH_2).CH : CH_2$$
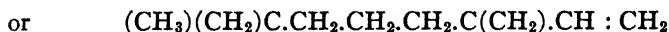
Its characters are as follows:

Sp. gr. 15.5°................................. 0.801
Ref. index 20°................................ 1.4700 at 19°
B. p........................................ 107°

It is easily oxidised and oils containing it frequently become far less soluble in alcohol, on keeping, owing to this fact.

Ocimene exists in Javanese basil oil. Its constitution is

$$CH_3.C(CH_3): CH.CH_2.CH: C(CH_3).CH: CH_2$$

and it has the following characters:

Sp. gr. at 15.5°................................. 0.803
Ref. index at 20°................................ 1.4850
B. p. at 750 mm. ............................... 172°

Ocimene has recently been found to the extent of 80% in the essential oil of *Homoranthus flavescens*, by A. R. Penfold. (*J. and Proc. Royal Soc. N. S. W.* 1923, **56**, 193).

## Constitution of the Dicyclic Terpenes

The structural formulæ of the dicyclic ketones are less clearly established than those of the monocyclic compounds. The following formulæ are generally accepted for pinene and its hydrochloride and for bornylene, and the recent work of Lipp, Komppa, Haworth and King has definitely settled the contitution of camphene. It should be noted that the formula shown for pinene hydrochloride is capable of existing in 4 modifications corresponding with *d-* and *l-*borneol and *d-* and *l-iso-*borneol, the existence of which are well established. The existence of these isomeric chlorides has been one of the chief difficulties in establishing the constitution and identity of various preparations having the formula $C_{10}H_{17}Cl$; *e. g.*, pinene hydrochloride probably consists mainly of *d-iso-*bornylchloride, but mixed with *d-*bornylchloride.

C—CH₃
HC CH
C(CH₃)₂
H₂C CH₂
CH
α-Pinene

C—CH₃
HClC CH₂
C(CH₃)₂
H₂C CH₂
CH
Pinene hydrochloride

C=CH₃
HC C(CH₃)₂
CH₃
H₂C CH
CH₂
Camphene
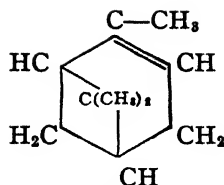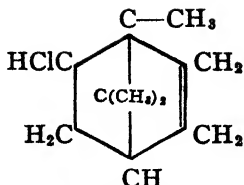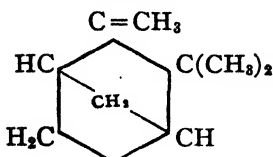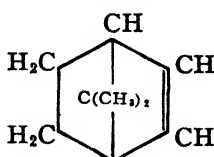
CH
H₂C CH
C(CH₃)₂
H₂C CH
C.CH₃
Bornylene

## Sesquiterpenes

These substances possess the formula $C_{15}H_{24}$, and many of them are found naturally in essential oils. Some of them have a distinct odour value in the essential oil, others are practically odourless, and by removing them the odour and solubility of the oils are increased. They are of very complicated constitution and their relationships are not yet so well understood as are those of the terpenes, although the present progress in this direction is very rapid. Three well defined groups are recognised—the monocyclic, bicyclic and tricyclic. It is true, within narrow limits, to say that the sp. gr. increases, and the molecular refraction increases as the number of closed rings in the molecule increases. Thus, the following limit figures are approximately true:

|  | MOLECULAR REF. | SP. GR. AT 15.5° |
|---|---|---|
| Minocyclic sesquiterpenes | 67.76 | 0.875–0.890 |
| Bicyclic sesquiterpenes | 66.15 | 0.900–0.920 |
| Tricyclic sesquiterpenes | 64.45 | 0.930–0.940 |

The most important of the sesquiterpenes are cadinene, caryophyllene, santalene, cedrene, gurjenene and zingiberene. These will be shortly described, and the characters of a number of less important sesquiterpenes summarised in the table on page 453.

## Cadinene, $C_{15}H_{24}$

This terpene owes its name to its occurrence in oil of cade, the product of the destructive distillation of juniper wood tar. It is,

however, found in numerous essential oils, for example, savin, patchouli, camphor, juniper, cedar wood, and others. Pure cadinene is obtained by saturating the fraction of oil of cade boiling at 260°–280° dissolved in ether, with dry hydrochloric acid gas. The hydrochloride, separated, recrystallised and dried, is distilled with aniline, and the regenerated cadinene then has the following characters:

Sp. gr. at 15.5°.............................. 0.922
Ref. index at 20°............................. 1.5070
Opt. rot..................................... −105° to −111°
B. p........................................ 271° to 275°

Cadinene yields a well marked colour reaction. If a few drops are dissolved in chloroform, and the mixture shaken with a few drops of concentrated sulphuric acid, a beautiful green colour is developed; this turns to dark green then olive, and on warming to a deep red.

Cadinene dihydrochloride, formed as above described, melts at 117° to 118°. The dihydrobromide melts at 124° to 125°, and the nitrosochloride at 93° to 94°.

### Caryophyllene, $C_{15}H_{24}$

This very important sesquiterpene, as usually described, is a mixture of two if not three, chemical individuals. The name caryophyllene is usually applied to the sesquiterpene or mixture of sesquiterpenes found in clove oil and other essential oils. As isolated from clove oil, it has the following characters:

B. p........................................ 258°–261°
Sp. gr. at 15.5°.............................. 0.905 to 0.910
Opt. rot..................................... −7° to −9°
Ref. index at 20°............................. 1.5010

Recent researches by Deussen and Lewinsohn (*Ann.*, **356,** 1; **359,** 245) and Semmler and Mayer (*Ber.*, 1911, **44,** 3657), indicate that there are at least four natural sesquiterpenes of the caryophyllene family, all having characters which, apart from optical rotation do not differ much from each other.

Caryophyllene dihydrochloride, $C_{15}H_{24}.2HCl$, is obtained by saturating an ethereal solution of the hydrocarbon, with dry hydrochloric acid gas. It melts at 69°–70°. The most characteristic compound for the identification of caryophyllene, is caryophyllenic alcohol $C_{15}H_{26}O$. The fraction containing the sesquiterpene is heated on the water bath, with about its own weight of sulphuric acid, twice its weight of water and forty times its weight of glacial

acetic acid. When the reaction is complete the mixture is steam distilled. The first portions are rejected, but when the distillate commences to solidify, it is collected and purified by recrystallisation from alcohol. It then melts at 94–96°. The nitrosochloride, prepared in the usual manner, melts at 158° to 163°.

In spite of the complex nature of the caryophyllene hydrocarbons, the melting points of the derivatives are very constant and serve for the identification of the hydrocarbon or mixture of hydrocarbons. Caryophyllene, probably, has the following formula:

$$\begin{array}{c} \text{CH(CH}_3\text{)} \quad \text{CH}_2 \\ \text{H}_2\text{C} \qquad \qquad \text{CH}_2 \\ \text{H}_2\text{C} \qquad \qquad \text{CH}_2 \\ \text{(CH}_3\text{)}_2\text{:C:C} \qquad \text{C}=\text{CH}_2 \end{array}$$
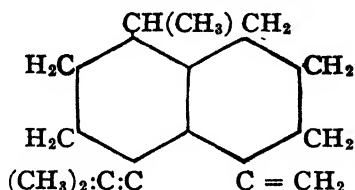
### Santalene, $C_{15}H_{24}$

Sandalwood oil, distilled from *Santalum album*, contains two isomeric sesquiterpenes, known as $\alpha$-santalene and $\beta$-santalene. It is doubtful whether they have been obtained in a state of absolute purity, but the characters for the purest specimens so far isolated lie between the following limits:

### $\alpha$-SANTALENE

B. p. at 10 mm.. ............................... 118°–120°
B. p. at 760 mm............................... 252°–254°
Sp. gr. at 15 5°.................................. 0.902–0.913
Opt. rot........................................ −3.5′ to −15°
Ref. index at 20°.............................. 1.4920

### $\beta$-SANTALENE

B. p. at 10 mm............................... 126°–130°
B. p. at 760 mm.............................. 261°–262°
Sp. gr. at..15.5................................ 0.895–0.899
Ref. index at 20°............................. 1.4930–1.4950
Opt. rot....................................... −35° to −41°

### Cedrene, $C_{15}H_{24}$

Cedrene forms the principal constituent of oil of cedar wood. It is a tricyclic sesquiterpene having the following characters:

B. p........................................... 262°–263°
Sp. gr. at 15.5°................................ 0.9354
Opt. rot....................................... −55°
Ref. index at 20°.............................. 1.5023

Cedrene yields no crystalline halogen derivatives, but on oxidation in acetone solution by potassium permanganate, cedrene glycol, $C_{15}H_{26}O_2$, melting at 160° is obtained. A very characteristic acid derivative has been obtained by Semmler and Risse (*Ber*, 1912, **45**, 355). If the fraction of an oil to be examined be oxidised by either permaganate or ozone, a keto-acid $C_{15}H_{24}O_3$ is obtained, which by further oxidation by alkaline solution of bromine, or nitric acid, yields cedrene-dicarboxylic acid melting sharply at 182–183°.

## Gurjunene, $C_{15}H_{24}$

Gurjunene is of particular interest, because it is one of the principal constituents of the essential oil of gurjun balsam. The balsam itself is used to a considerable extent for the adulteration of copaiba balsam, and the essential oil has been used to adulterate peppermint oil, palmerosa oil and various other essential oils. It can be readily detected by the following colour reaction. If a few drops of the suspected oil be mixed with 10 c.c. of glacial acetic acid containing 5 drops of nitric acid, a mauve-pink to deep violet colouration results within 30 seconds.

Gurjunene consists of two isomeric sesquiterpenes, $\alpha$-gurjunene, and $\beta$-gurjunene, which have been isolated by Deussen and Philipp (*Ann.*, 1910, **374**, 105). The former has not been prepared in a pure condition, but boils at about 119° at 112 mm., and has an optical rotation of not less than −61°.

$\beta$-Gurjunene has the following characters:

B. p. .................................... 113°–114° at 7 mm.
Sp. gr. at 15.5° ........................ 0.933 at 20°
Ref. index at 20° ....................... 1.5052
Opt. rot. ............................... +19° (or over).

Both gurjunenes yield, on oxidation, the same ketone $C_{15}H_{24}O$ which forms a semicarbazone melting at 234°.

## Zingiberene, $C_{15}H_{24}$

This sesquiterpene is a constituent of the essential oil of ginger. It has the following characters:

B. p. .................................... 270°
B. p. at 32 mm. ......................... 160°–161°
Sp. gr. at 15.5° ........................ 0.873 at 20°
Ref. index at 20° ....................... 1.4940
Sp. rot. ................................ −73° (approximately)

It forms a crystalline hydrochloride, when its solution in an equal volume of glacial acetic acid is saturated at 0° with dry HCl. This

substance melts at 168°–169°. It also forms a nitrosochloride, which is prepared in the same manner as pinene nitrosochloride, and melts at 96°–97°.

The nitrosate $C_{15}H_{24}.N_2O_4$ is formed when equal volumes of zingiberene and glacial acetic acid are cooled to 0°, and ethyl nitrite, and then nitric acid added. The nitrosate is dissolved in ethyl acetate, and precipitated by alcohol. It melts at 97°–98°.

The constitutions of the sesquiterpenes are, with few exceptions, still unsettled. Ruzicka and Stoll (*Helv. Chim. Act.*, 1922, **5,** 345, 369, and 923) have published the latest speculative work on the subject, and from their researches it appears probable that they fall into two main groups: (1) Those of the cadalin type. Cadalin, $C_{15}H_{18}$ a hydrocarbon closely related to naphthalene, has been synthesised by these chemists and they consider that cadinene, calamene, copa-ene, and zingiberene are based on the cadalin nucleus. (2) Those of the eudalin type. Eudalin, $C_{14}H_{16}$, is also a naphthalene derivative, but its structure is not yet settled. Santalene and selinene are members of this group.

## CHARACTERS OF SESQUITERPENES

| Sesquiterpene | B. p. | Sp. gr. at 15.5° | Rotation | Ref. index at 20° | Crystalline derivatives |
|---|---|---|---|---|---|
| Aromadendrene... | 260°–265° | 0.923 | ± 4.7° | 1.4964 | ........................ |
| Bisabolene........ | 261°–262° | 0.880 | ±41° | 1.4901 | Trihydrochloride, m. p. = 79°–80° |
| Calamene........ | 123°–126° at 10 mm. | 0.922 | + 5° | 1.5057 | ........................ |
| Copaene.......... | 119°–120° at 10 mm. | 0.9087 | −13° 35′ | 1.4894 | Yields cadinene hydrochloride, m. p. = 117°–118° |
| Clovene.......... | 259°–260° | 0.926 | + 2.84° | 1.4992 | ........................ |
| Eudesmene....... | 129°–132° at 10 mm. | 0.923 | +49° | 1.5074 | Dihydrochloride, m. p. = 79°–80° |
| Herabolene....... | 130°–136° at 16 mm. | 0.947 | −14° 12′ | 1.5125 | Dihydrochloride, m. p. = 98°–99° |
| Humulene........ | 263°–266° | 0.900 | 0° | ........ | Nitrosochloride, m. p. = 164°–165° Nitrosate, m. p. = 162°–163° |
| Longifolene....... | 254°–256° at 706 mm. | 0.928 at 30° | +42.7° | 1.4950 at 30° | Hydrochloride, m. p. = 59°–60° |
| Patchoulene: | | | | | |
| (a)............. | 264°–265° | 0.933 | −58° 45′ | ........ | ........................ |
| (b)............. | 273°–274° | 0.930 | + 0° 45′ | ........ | ........................ |
| Selinene.......... | 268°–272° | 0.923 | +49° 30′ | 1.5048 | Dihydrochloride, m. p. = 72°–74° (Selinene is probably a mixture of two isomers with slightly different characters.) |
| Vetivene: | | | | | |
| (a) Tricyclic.... | 128°–130° at 16 mm. | 0.939 | −12° 16′ | 1.5113 | ........................ |
| (b) Bicyclic..... | 137°–140° at 16 mm. | 0.9355 | −10° 12′ | 1.5190 | ........................ |

## Diterpenes and Polyterpenes

These hydrocarbons are formed by the action of heat or polymerising agents on isoprene and the terpenes. They are not further polymerised by sulphuric acid, and combine with smaller proportions of hydrochloric acid than the unpolymerised terpenes. Their chemical characters have been little studied.

**Colophene,** $C_{20}H_{32}$, or $(C_5H_8)_4$, is produced in considerable quantity when turpentine oil is agitated with strong sulphuric acid or phosphoric anhydride, and is present in rosin oil. It is a very viscid liquid of 0.939 sp. gr., which begins to boil at about 318°, and exhibits a strong blue fluorescence. It forms an unstable hydrochloride. Antimony trichloride converts turpentine oil into a colophene from which absolute alcohol extracts a liquid, leaving solid *tetraterebenthene*, $C_{40}H_{64}$ as an amorphous mass, soluble in ether, carbon disulphide, benzene, or turpentine, and melting above 100°. It is converted into liquid colophene by distillation.

The oils of black pepper, copaiba, and gurjun balsam contain a diterpene, or mixture of that nature, b. p. 250° to 260°. The compound has not been obtained in a state of purity.

**Diterpilene,** isomeric with colophene, is produced when oil of turpentine is heated with absolute formic acid. It is a thick oily liquid, optically inactive and smelling like copaiba balsam. It has a sp. gr. of 0.9404 at 0°, and resinifies on exposure to air.

## The Estimation of Hydrocarbons

The determination of terpene and sesquiterpene hydrocarbons has assumed considerable importance on account of the large and growing employment of terpeneless and sesquiterpeneless essential oils.

Very few commercial samples of such oils are absolutely free from either terpenes or sesquiterpenes, but some specimens contain so much of one or both types of hydrocarbons, that their estimation becomes a matter of importance. Bocker (*J. prakt. chem.*, 1914, **89,** 199), taking terpeneless oil of lemon as the basis of his experiments gives the following method for carrying out this estimation. Sufficient of the oil is first deprived of its citral by extraction in the usual way with sodium sulphite, to leave about 6 c.c. of residual unabsorbed oil. Of this 5 c.c. is taken and mixed in a separator of

from 600 to 700 c.c. capacity, with 500 c.c. of alcohol (51% by volume), at a temperature of 0° or a few degrees under. The mixture, kept at this temperature is well shaken for some time. The oxygenated substances present are dissolved by the alcohol, and the hydrocarbons left behind almost quantitatively. The separator is allowed to stand in a cooling bath at 0° for 6 to 10 hours, and when separation is complete (which may not be for two days), the lower layer is drawn off to about 10 c.c. and any oil drops which may be adherent to the sides of the separator are rinsed down with a little more 51% alcohol at 0°, and when the whole of the oil drops have coalesced, the undissolved oil is run out into a tube graduated to 0.1 c.c, and measured (the last drops may be washed out with cold 51% alcohol and the whole measured above the alcohol). If it is necessary to approximately estimate the relative amounts of terpenes and sesquiterpenes, 100 to 200 c.c. of the original oil are first fractionally distilled *in vacuo*. Those portions distilling over, and on examination of each 10 c.c. yielding dextrorotatory fractions, contain substantially all the terpenes whilst the undistilled fraction contains the sesquiterpenes. Each portion is separately freed from citral, and the hydrocarbons separately determined in each portion.

## (B) ALCOHOLS

A large number of alcohols are found naturally in essential oils. There are also a number of alcohols, which are either not found naturally, or if so, to a very limited extent, but which are prepared artificially, and are used to so great an extent in perfumery and in the manufacture of artificial or so called "synthetic" essential oils, that it is practically impossible to separate them from the natural alcohols in any systematic treatment.

### (a) Alcohols of the Methane and Allied Series

*Methyl alcohol*, $CH_3OH$ is a liquid of sp. gr. 0.810 and boils at 64°. It is soluble in water, and therefore, when present in essential oils is always washed out into the distillation waters. It forms, however, the alcoholic base of many important esters of essential oils, such as methyl salicylate, methyl anthranilate etc.

*Ethyl alcohol*, $C_2H_5OH$ is a liquid of sp. gr. 0.794 at 15.5° and boils at 78°. The remarks made under methyl alcohol apply to ethyl alcohol.

*Isobutyl alcohol* $(CH_3)_2.CH.CH_2OH$ is a liquid of sp. gr. 0.800 at 15.5° and boils at 108.5°.    It is found in the distillation waters.

*Isoamyl Alcohol* $(CH_3)_2.CH.CH_2CH_2OH$ is a liquid, b. p. 131°. It has been found in geranium, lavender and peppermint oils.

*Hexyl alcohols.*    Normal hexyl alcohol $CH_3(CH_2)_4CH_2OH$ exists in the form of esters in the oil of *Heracleum giganteum.*    It is a liquid of sp. gr. 0.824 at 15.5° and b. p. 157°.    Isohexyl alcohol $(C_2H_5)$ $(CH_3)CH.CH_2.CH_2.OH$ is the alcoholic base of the esters of Roman chamomile oil.    It is an oil of sp. gr. 0.829, sp. rot. +8.2°, and b. p. 154°.

*Heptyl alcohol*, $CH_3(CH_2)_4CH(CH_3)OH$ occurs in oil of cloves. It is an oil of sp. gr. 0.824 at 15.5° and b. p. 158°.

*Octyl alcohol*, $CH_3(CH_2)_4CH(C_2H_5)OH$, or ethyl-amyl-carbinol is a constituent of Japanese peppermint oil.    It is an oil of specific gravity 0.8247 at $\frac{20°}{40}$ b. p. 173–174° and has an optical rotation +6.8°.    Normal octyl alcohol, of the constitution $CH_3(CH_2)_6-CH_2OH$ has not been found in essential oils naturally, but has an odour recalling that of opoponax, and is used in the manufacture of blended perfumes.    It is an oil, b. p. at 196°–197° and has a sp. gr. 0.828 at 15.5°.

*Nonyl alcohol* $CH_3(CH_2)_7CH_2OH$ is an artificially prepared alcohol with a marked odour of roses, with a suggestion of orange.    It is an oil of sp. gr. 0.840 at 15.5°, ref. index 1.4358 at 20°, and b. p. 101°–102° at 12 mm.    It is of great value in perfumery.

*Decyl alcohol*, $CH_3(CH_2)_8CH_2OH$ is also an artificially prepared alcohol, and is probably the most useful of the higher aliphatic alcohols for perfumery purposes.    It is an oil, b. p. 110° at 13 mm. Its odour is floral, and it is of great service to the modern perfumer.

*Undecylic alcohol*, $CH_3(CH_2)_9CH_2OH$ occurs in Algerian oil of Rue, but is also manufactured artificially.    It boils at 231° to 233°. It resembles decylic alcohol in odour with a slight variation.

*Undecylenic alcohol* $CH_2:CH(CH_2)_8.CH_2OH$ closely resembles decyl alcohol in general characters, and is of considerable value to perfumers.    It boils at 128° at 13 mm.

## (1) THE GERANIOL GROUP

There exist in many essential oils several alcohols and their allied aldehydes, which are of the very highest value in perfumery, and

which were, in the last edition of this work, described as olefinic terpene alcohols and aldehydes. This name appears to have little if anything to justify it, and as they are very few in number they may be better classified under the name of the principal member of the series, viz., geraniol.

They are open-chain compounds of intense and fine odour.

From time to time various alcohols have been described as belonging to this series, but on careful examination most of them has been found to be other than a mixture of two or more of the above compounds. Such are coriandrol, from oil of coriander, which is merely impure linalol; nerolol from oil of neroli, which is identical with linalol; rhodinol, from rose oil, which appears to be a mixture of geraniol and citronellol; and so on.

### Geraniol, $C_{10}H_{17}.OH$

Geraniol is a monatomic primary open-chain alcohol, isomeric with linalol, which is a tertiary alcohol. The following formula probably expresses its constitution:

$$(CH_3)_2C:CH.CH_2.CH_2.C(CH_3):CH.CH_2OH$$
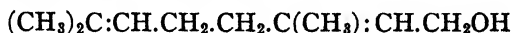
It is however, possible that its constitution is

$$\begin{array}{c} H_3C \\ \diagdown \\ \quad\quad C.CH_2.CH_2.CH_2.C(CH_3):CH.CH_2OH \\ \diagup\diagup \\ CH_2 \end{array}$$
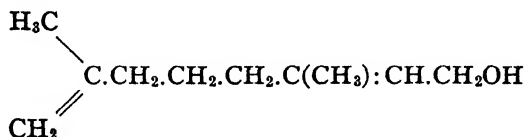
Geraniol is the principal constituent of true geranium oil, and of the oil of palmarosa, or so-called "Turkish geranium." It is also one of the chief constituents of rose oil, and is present to a considerable extent in citronella oil and in smaller proportions in the oils of lavender, lemon-grass, and other oils.

Geraniol may be isolated from oils containing not less than 25% by converting it into its crystalline compound with calcium chloride, $(C_{10}H_{18}O)_2,CaCl_2.$[1]

---

[1] For the production of this substance, the oil, previously dried by anhydrous sodium sulphate, is intimately mixed in a mortar with an equal weight of recently fused calcium chloride. The mixture is kept in a desiccator for 24 hours, at or below 0°, and is then triturated with dry spirit or petroleum spirit. The liquid portion is separated by a suction filter and the crystalline mass treated with water, when the compound is decomposed and the liberated geraniol separates as an oily layer. This is separated and redistilled under reduced pressure.

Geraniol may be prepared on a commercial scale (*German Patent*, No. 80,007) by distilling geranium or pelargonium oil under reduced pressure (14 mm.), and heating the fraction which distils between 120° and 130° in an autoclave with acetic anhydride. The resulting esters are fractionated, distilled, the fraction passing over between 127° and 132° (consisting chiefly of geranyl acetate) saponified with alkali, and the liberated geraniol fractionated *in vacuo*. The portion distilling between 120° and 125° consists essentially of geraniol and forms the "rhodinol" of commerce.

As prepared by the foregoing methods, geraniol always contains more or less citronellol, from which it may be separated by converting it into acid geranyl phthalate in the manner prescribed by Flatau and Labbé (page 596).

Commercial geraniol prepared from citronella oil frequently contains traces of citronellal, which ruins its odour.

Geraniol is a colourless oil, with a sweet rose-like odour, but lacking the fine odour of the oils in which it is an essential constituent. By careful oxidation with chromic acid it yields aldehyde citral, and by heating with water in an autoclave to 200°, it is partly converted into its isomer linalol. Its esters are sweet-smelling liquids, and form important consitutents of many essential oils. Geranyl acetate is a fragrant oil of sp. gr. 0.9174 and refractive index 1.4628. It boils at 129° at 16 mm. Geranyl tiglate forms the principal constituent (with free geraniol), of pelargonium leaf oil (true geranium oil).

Geraniol has the following characters:

Sp. gr at 15.5°............................ 0.880  to 0.883
Opt. rot.................................... ±0°
Ref. index at 22°.......................... 1.4766 to 1.4786
B. p....................................... 228° to 230°

Tiemann and Kruger recommend the following method for the purification of impure geraniol. It is treated with sodium, and the alcoholate is then treated with ether and phthalic anhydride, by which it is converted into geraniol-sodium-phthalate, which is hydrolysed by alkali hydroxide, and the pure geraniol precipitated by the addition of water.

Jacobsen detects geraniol in essential oils as follows:

The oil—or fractions boiling at 225° to 235°, so that at least 25% is present—is well mixed with an equal weight of dry powdered

calcium chloride and the mixture kept in a desiccator at $-4°$ for 12 to 16 hours.   If the geraniol is present in the form of esters, it is of course saponified first.

The soft mass is rubbed with dry benzene, ether, or petroleum spirit and the liquid portion removed by a suction filter.   The calcium chloride compound of geraniol is then treated with water, the oil separated, washed, and distilled under reduced pressure, when geraniol passes over at $230°$.

Erdmann (*J. pr. Chem.*, 1897, [ii], **56,** 1) prefers to identify geraniol by treating it with diphenyl-carbamic chloride and pyridine on a water-bath.   A current of steam removes diphenylamine and unaltered compounds, and the geraniol diphenyl-urethane is recrystallised from alcohol.   It then melts at $82.2°$.

Geraniol may be prepared from citral (geranaldehyde) by treating an alcoholic solution of that substance, feebly acidified with acetic acid, with sodium amalgam.   To obtain a pure product, the solution should be heated with alkali to decompose unaltered citral, and steam-distilled, rejecting the last portions of the distillate.

On treatment with chromic acid mixture, geraniol is converted into *citral* or *geranial*, and on oxidation with permanganate it yields *isovaleric acid*.   Dehydrating agents convert geraniol into inactive *terpenes*.

By heating with acid anhydrides, geraniol is readily converted into the corresponding *esters*.   Conversion into geranyl benzoate and acid phthalate is used for the purification of geraniol.   Treatment with phthalic anhydride affords a sharp distinction between geraniol and linalol, the former being converted into an acid phthalate while the latter is not attacked (see under Linalol).

F. Tiemann (*Ber.*, 1898, **31,** 2989) states that when geraniol is heated with very strong alcoholic potassium hydroxide to $150°$ for eight hours, it is hydrolysed with formation of ethyl alcohol and *methyl-heptenol*, $(CMe_2:CH.CH_2.CH_2.CHMe.OH)$.[1]   This compound boils at $85°$ to $86°$ under a pressure of 15 mm., and at $175°$ to $176°$ at the ordinary atmospheric pressure.   Linalol remains almost unchanged when heated with strong alcoholic potassium hydroxide.

According to H. and E. Erdmann (*J. prakt. Chem.*, 1897, **56,** 1), if 1 drop of geraniol ("rhodinol") be diluted with 5 c.c. of alcohol, and 10 drops of strong sulphuric acid added without shaking, the

[1] According to P. Barbier, *dimethyl-heptenol* is the product of the reaction.

acid sinks and takes an intense orange-yellow colour, while on gently moving the vessel the colour turns to reddish-violet at the surface of the junction of the two liquids. Linalol shows a similar reaction, but the colour is less stable and readily changes to brown. Citronellol gives a feebler colouration of a bluish tint.

**Commercial Geraniol.**—Eckart orginally described the mixture of liquid alcohols from rose oil by the name of *rhodinol*, but it is now agreed that these and similar products consist essentially of geraniol with more or less citronellol etc. which, if not separated by special means, is always present in commercial geraniol.[1] The name rhodinol is applied commercially to the product from geranium oil and other sources. True rhodinol will be discussed under citronellol.

By the action of dilute acids, many of the derivatives of geraniol are converted into cyclic isomerides of the same molecular weights, having lower b. p., higher sp. gr., and somewhat lower indices of refraction than the open-chain compounds from which they are derived.

### Linalol (Linalool), $C_{10}H_{17}.OH$

Linalol is a monatomic open-chain alcohol, isomeric with geraniol, from which it differs in being optically active. Linalol is the essential constituent of oil of linaloe, and also exists, in the free state or in the form of esters, in the oils of petitgrain, bergamot, coriander, lavender, neroli, *Asarum Canadense*, etc.

Linalol exists in both the dextrorotatory and the lævorotatory forms. It is doubtful whether either form has been prepared in a state of absolute purity, so that the exact optical activity is unknown. Numerous specimens have been examined. The figures generally represent a very impure product, but the following may be taken as the approximate values for the alcohol: Sp. gr. at 15°, 0.872 optical rotation, about ± 20°: refractive index at 20°, 1.4650, and b. p. 197° to 199° at ordinary pressure or 85° at 12 mm.

It is a colourless oil with a sweet odour, and forms an acetate which also exists in bergamot and lavender oil to a considerable extent. The acetate is the typical odour-bearer in oil of bergamot, and that oil is rightly valued on its content of this ester. Linalyl acetate, $C_{10}H_{17}O.$-

---

[1] Varieties of geraniol also result from the practice of distilling the liquid over different flowers, to obtain products described as rose-geraniol, mignonette-geraniol, etc., some of which are greatly preferable as perfumes to ordinary geraniol.

$COCH_3$, has a sp. gr. 0.912 and b. p. 105° to 108° at 12 mm.   It can be prepared artificially by the action of acetic anhydride on linalol, and the artificial ester is an important commercial article, especially at times when bergamot oil is very scarce.

Linalol is a tertiary open chain alcohol of one of the two alternative formulæ

$$CH_3 \\ \phantom{CH_3}\searrow C:CH.CH_2.CH_2.C(CH_3)OH.CH.CH_2 \\ CH_3 \nearrow$$

or

$$CH_3 \\ \phantom{CH_3}\searrow C.CH_2.CH_2.CH_2C(CH_3)OH.CH:CH_2 \\ CH_2 \nearrow$$
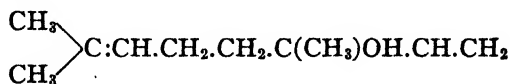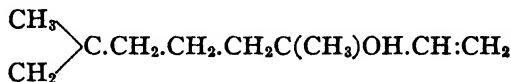
Bethal, however (*Comptes rendus* 1919, **168,** 945) considers it to be an oxide, resembling a lactone.   The difficulty of purifying linalol is the reason that its optical activity is still a matter of some doubt.   The following are the figures of the purest specimens which have been obtained from the essential oils quoted:

|  | B. P. | SP. GR. AT 15.5° | REF. IND. AT 20° | OPT. ROT. |
|---|---|---|---|---|
| Lavender | 197°–199° | 0.872 | 1.4640 | −10° 35′ |
| Bergamot | 197°–199° | 0.872 | 1.4629 | −16° |
| Linaloe | 197°–200° | 0.877 | 1.4630 | −2° |
| Lime | 198°–199° | 0.870 | 1.4668 | −20.7° |
| Orange | ......... | ..... | ...... | +19.8° |

Schimmel & Co. consider 0.8666 to be the correct specific gravity of pure linalol.   Optically inactive linalol results by heating geraniol in an autoclave at 200°, or by treating geraniol with hydrochloric acid, and decomposing the resulting chloride with alcoholic potash.

Linalol may be characterised by its urethane melting at 65°; its naphthyl-urethane melting at 53°, or by its oxidation to citral.

Linalol yields, among other products, some citral on oxidation.

Linalol is one of the alcohols that cannot be quantitatively estimated by acetylation, as decomposition takes place during the process (see under Estimation of Free Alcohols).

Linalyl acetate is also a constituent of oil of petitgrain.

By treatment with hydrochloric acid, linalol yields liquid *chlorides*, containing $C_{10}H_{18}Cl_2$, which has an odour like that of camphor,

and by distillation with lime yields a *terpene* of characteristic odour boiling at 168° to 172°.  Linalol combines with 4 atoms of bromine.

By treating linalol with acetic anhydride, and saponifying the linalyl acetate formed, Barbier obtained a product which he named licarhodol.  K. Stephan (*J. pr. Chem.*, 1898, **58,** 109) states that a strongly dextrorotatory, crystalline terpineol is formed under these conditions, and that Barbier's product was probably a mixture of this terpineol with linalol and geraniol.  Stephan states that acetic acid does not act on linalol till the mixture is warmed, whereas concentrated formic acid readily converts lævo-linalol into dextro-terpineol, and dextro-linalol into lævo-terpineol.

According to H. E. Burgess (*Analyst*, 1900, 265), linalol gives an immediate deep violet coloration when shaken with 2 or 3 times the quantity of a 10% solution of mercuric sulphate in 25% sulphuric acid.

**Nerol.**—This alcoholic substance was discovered in oil of neroli by Hesse and Zeitschel.  The oil was freed as far as possible from geraniol by means of calcium chloride, and the phenylurethanes of the residuary alcohols were prepared.  By fractional crystallisations, the nerol compound was obtained in a state of purity, and from it the alcohol was liberated in the usual manner.

Nerol is isomeric with geraniol and linalol, $C_{10}H_{17}OH$, and has a sp. gr. 0.8813 at 15.5°, is optically inactive, and boils at 225° at ordinary pressure, and at 125° at 25 mm.  Its diphenylurethane melts at 52° to 53°, which enables it to be sharply differentiated from geraniol.  The relations between nerol and geraniol are almost certainly stereoisomeric, their probable configurations being as follows:

$$CH_3.C.CH_2.CH_2.CH:C(CH_3)_2 \qquad CH_3.C.CH_2.CH_2CH:C(CH_3)_2$$
$$\| \qquad\qquad\qquad \|$$
$$HC.:CH_2OH \qquad\qquad CH_2(OH)C.H$$
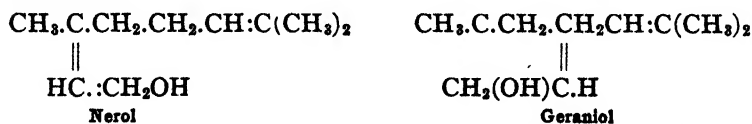
Nerol                    Geraniol

Their corresponding aldehydes are probably *a*-citral (geranial) and *b*-citral (neral).

## Citronellol and Rhodinol, $C_{10}H_{19}.OH$

Citronellol is an open-chain alcohol closely related to geraniol, from which it differes in formula by 2 atoms of hydrogen.  It occurs in association with geraniol in rose oil, geranium oil, etc., and is

also obtainable by the reduction of its aldehyde, citronellal,[1] which occurs in oil of citronella, etc.

For many years it has been a matter of controversy as to whether the alcohol originally known under the name rhodinol is a chemical individual or not. The commercial article was undoubtedly a mixture containing much geraniol and for many years it was accepted that rhodinol was in fact only a mixture of geraniol and citronellol. Today, however, there appears to be very considerable evidence in favour of the existence of an iosmer of citronellol, which was always present in commercial rhodinol, and for which the name rhodinol is properly retained.

The following may be taken as the constitutions of the two isomers

$$\begin{array}{c} CH_2 \\ \diagdown \\ \diagup \\ CH_3 \end{array} C.CH_2\ CH_2.CH_2.CH(CH_3)CH_2.CH_2OH$$

<div align="center">Citronellol</div>

$$\begin{array}{c} CH_3 \\ \diagdown \\ \diagup \\ CH_3 \end{array} C:CH.CH_2.CH_2.CH(CH_3)CH_2\ CH_2\ OH$$
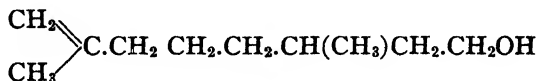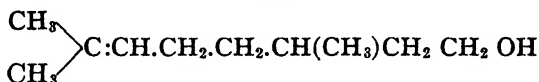
<div align="center">Rhodinol</div>

Barbier and Locquin (*Comptes rendus* **157**, 1114) started from the two isolated substances *d*-citronellol and rhodinol, attached HCl to both, and as might be expected from an examination of the formulæ, the same additive compound was obtained. On elimination of the HCl, rhodinol is regenerated, and not citronellol.

Rhodinol can also be obtained directly from citronellal by conversion into the oxime, nitrile, thence to citronellic acid. When this is treated in benzene solution with thionyl chloride a chlorinated acid results which is converted by alcohol into the hydrochloride of ethyl rhodinate. Boiling with sodium acetate converts this into ethyl rhodinate, which is reduced to rhodinol by sodium and alcohol.

Further evidence as to the difference between citronellol and rhodinol is yielded by the fact that rhodinal the aldehyde derived from rhodinol, does not yield the same derivatives as does citronellal.

---

[1] Citronellol is not obtainable by direct action of nascent hydrogen on geraniol. If, however, a olution of geranic acid in boiling amyl alcohol be treated with sodium, citronellic acid is obtained, and when a mixture of calcium citronellate and formate is subjected to dry distillation citronellal is formed, which can be reduced to citronellol by treatment in alcoholic solution with sodium amalgam. The compounds obtained by the foregoing processes are optically inactive.

Harries and Comberg (*Ann.*, 1915, **410**, 1) have shown that so called natural "citronellal" obtained from citronella oil consists of about 40% citronellal and 60% rhodinal, and H. J. Prins has suceeded in isolating the two isomerides in a pure state (*Chem. Weekblad*, 1917, **14**, 692).

It is clear that the physical characters usually attributed to these alcohols must be taken as being approximate only, as they are, in every case, almost certain to be mixtures. The following may be taken as the nearest available figures for citronellol or rhodinol, according to origin:

### FROM OTTO OF ROSE

B. p. at 15 mm. ................................. $113°–114°$
Sp. gr. at 20° .................................. 0.8612
Ref. index at 20° ............................... 1.4579
Opt. rot. ...................................... $-4° 20'$

### FROM GERANIUM OIL

B. p. at 764 mm. ............................... $225°–226°$
Sp. gr. at 15° .................................. 0.862
Ref. index at 22° ............................... 1.4561
Opt. rot. ...................................... $-1° 40'$

### FROM CITRONELLA OIL

B. p. at 7 mm. ................................. $109°$
Sp. gr. at 15° .................................. 0.872
Ref. index at 20° ............................... 1.4629
Opt. rot. ...................................... $+2° 32'$

### FROM BAROSMA PULCHELLA OIL

B. p. at 5–6 mm. ............................... $117–118°$
Sp. gr. at 17.5° ................................ 0.8565
Ref. index at 17.5° ............................. 1.4566
Opt. rot. ...................................... $+4°$

Citronellol yields citronellyl-phthalate of silver, by heating equal quantities of phthalic anhydride and citronellol on a water bath for an hour. The mixture is well washed with hot water several times, and ammonia is added. Neutral compounds are then extracted by ether, and the ether separated. The residual liquid is dissolved in alcohol, and precipitated with a normal solution of $AgNO_3$. The crystals separating are washed with alcohol, then with ether, and dried *in vacuo*. They then melt at $125°–126°$.

Both citronellol and geraniol have sweet rose odours and are employed in the manufacture of artificial otto of rose.

## Methyl-heptenol, $C_8H_{16}O$

This is an open chain alcohol, found in Mexican and Cayenne linaloe oil. It may also be prepared by the reduction of the ketone methyle-heptenone. Its odour is delicate, resembling that of the rose. It has the following characters:

```
Sp. gr. at 15.5°................................. 0.858
Ref. index at 20° ............................... 1.4495
B. p. .......................................... 178°–180°
Opt. rot. ....................................... −1° 34′
```

## Bupleurol, $C_{10}H_{20}O$

Bupleurol is an open chain alcohol, isolated from the essential oil of *Bupleurum fruticosum* by Francesconi and Sernagiotto (*Gazz Chim. Ital.*, 43, 1, 153). It is a sweet smelling oil of rose odour, having the following characters:

```
B. p............................. ................... 210°
Opt. rot........................................... 0°
Ref. index at 20° .................................. 1.4508
Sp. gr. at 15.5°................................... 0.850
```

It yields a phenyl-urethane melting at 45°.

## Androl, $C_{10}H_{20}O$

Androl is an alcohol isolated from oil of water fennel and has a distinct odour of that plant.

Its characters are as follows:

```
B. p. .......................................... 197°–198°
Sp. gr. at 15.5°................................. 0.858
Opt. rot. ....................................... −7° 10′
Ref. index at 20° ............................... 1.4499
```

It yields a phenyl-urethane melting at 42°–43°.

## Farnesol, $C_{15}H_{26}O$

Farnesol is an open chain alcohol, which, because of its percentage formula has been called an "aliphatic sesquiterpene alcohol." It has been found in many flower oils, such as lime flowers, cassie, lilac, and mignonette. It also occurs in the oil from ambrette seeds.

It has a very faint odour when smelt in bulk, but when allowed to evaporate slowly a beautiful lily-of-the-valley perfume is appar-

ent.    Prepared from ambrette seeds, in which it occurs to the extent of about 0.1%, it has the following characters:

    B. p. at 10 mm. .................................... 160°
    Sp. gr. at 15.5°...................................... 0.887
    Opt. rot. ........................................... 0°
    Ref. index at 20° ................................... 1.4881

When oxidised gently by means of potassium dichromate it yields the aldehyde farnesal, an oil with a characteristic perfume, which forms a crystalline semicarbazone melting at 133°–135°, and which is particularly suitable for the identification of farnesol.

Farnesol has the constitution:

$$CH_3{\Large\diagdown} \atop CH_3{\Large\diagup}} C:CH(CH_2)_2.C(CH_3):CH(CH_2)_2C.(CH_3):CH.CH_2OH.$$
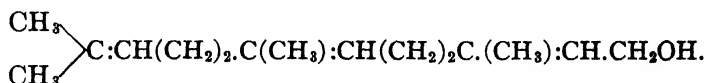
Farnesol has been stated to be responsible for the characteristic odour, known as the "honey" odour of otto of rose.    But this is not correct—the honey odour is due to the presence of traces of phenyl-acetic acid.

When dehydrated by potassium bisulphate, farnesol yields a sesquiterpene, which has been named farnesene.

## Nerolidol, $C_{15}H_{26}O$

This alcohol is also one of those known as the aliphatic sesquiterpene alcohols.    It exists in the higher boiling fractions of orange-flower oil.    Its characters are only approximately settled, as it is doubtful whether it has yet been isolated in a state of purity.    It has been prepared by Hesse, by Schimmel, and probably by Thoms who described it under the name peruviol, as he obtained it from Balsam of Peru oil.    These preparations had the following characters:

|  | B. p. | Sp. gr. at 15.5° | Opt. rot. | Ref. index at 20° |
|---|---|---|---|---|
| Ruzicka........ | 97° at 0.2 mm. | 0.880 | +13° | 1.4800 |
| Thoms......... | 140° at 7 mm. | 0.886 | +13° | ............ |
| Schimmel 1.... | 133° at 7 mm. | 0.882 | +14° | ............ |
| Schimmel 2.... | 127° at 4 mm. | 0.899 | +12° | 1.4898 |
| Schimmel 3.... | 127° at 5 mm. | 0.880 | +13° | 1.4802 |
| Hesse.......... | 129° at 6 mm. | 0.880 | +14° | ............ |

Nerolidol yields a phenyl-urethane melting at $37°$–$38°$, when allowed to stand for a month in contact with phenyl-isocyanate.

It is probable that Thoms' peruviol was a mixture of nerolidol, benzyl alcohol, and an alcohol not yet identified.

Ruzicka (*Helv. Chim. Acta*, 1923, **483**, 492) has confirmed the identity of peruviol with nerolidol and has prepared it in quantity by the following method. Five kilos of balsam of Peru were dissolved in three equal portions each in 1.5 litres of alcohol. The combined solutions were well shaken with 800 gr. of potassium hydroxide solution (3 parts of KOH to 2 parts of water) and warmed for several hours on a water bath. Alcohol was then removed by steam and the residue was extracted with ether. The extract was fractionated in a high vacuum and 94 grm. of nerolidol (boiling at $98$–$102°$ at 0.4 mm.) were obtained. It yielded a phenylurethane melting at $37°$. Nerolidol has the following constitution:

$(CH_3)_2{:}CH.CH_2.CH_2.C(CH_3){:}CH.CH_2.CH_2.C(CH_3)(OH).CH{:}CH_2$

## (2) BENZENE ALCOHOLS

### Benzyl Alcohol, $C_6H_5.CH_2OH$

This alcohol, which is the lowest member of the simplest aromatic series is found, principally in the form of esters, in numerous essential oils. It is usually found as benzyl acetate, benzyl benzoate and benzyl cinnamate, in such floral oils as those of jasmin, tuberose, cassia and ylang-ylang. It is, of course, also prepared artificially, both in the free state and in the form of esters, as an aid to the manufacture of artificial perfume. Its odour is not strong, but it is very sweet and is useful in numerous floral bouquets.

Its characters are as follows:

B. p. .............................................. $205$–$207°$
Sp. gr. at $15.5°$................................... $1.0435$
Opt. rot. .......................................... $0°$
Ref. index at $20°$ ................................. $1.5380$

It yields a phenyl-urethane melting at $77$–$78°$. The principal esters of benzyl-alcohol, which are much in demand by the perfumer, will be described under the section on esters.

### Phenyl-ethyl Alcohol

Phenyl-ethyl alcohol $C_6H_5.CH_2.CH_2OH$, is an alcohol which is very soluble in water, so that it is only found in traces in commercial

essential oils, as it is dissolved in the distillation waters. It has a marked odour of roses, and the fact that it is dissolved by the rose water out of the essential oil, the otto of rose of commerce, accounts for the fact that otto of rose, in spite of its beautiful odour, does not exactly represent the perfume of the rose.

Phenyl-ethyl alcohol is a substance which, although it occurs naturally in a number of essential oils, is manufactured artificially on a large scale, and is a regular commercial article. Its characters are as follows:

Sp. gr. at 15.5°............................ 1.0242
Ref. index at 20° ........................ 1.5321
B. p.................................... 220°–222° at 740 mm.
Opt. rot................................ 0°

It yields a diphenyl-urethane melting at 100°, by which it can be identified.

It is prepared, for example, by allowing phenyl-ethyl acetate, dissolved in four times its weight of absolute alcohol, to fall in drops on 6 times its molecular equivalent of sodium. The mixture is heated on a water bath for several hours until the sodium has disappeared. Water is added, the mixture is saponified and the free phenyl-ethyl alcohol distilled over in a current of steam.

Phenyl-ethyl alcohol is indispensable in the manufacture of artificial otto of rose, and is most useful in blending with many other floral perfumes.

### Phenyl-propyl Alcohol

Phenyl-propyl alcohol $C_6H_5.CH_2.CH_2.CH_2OH$, also known as hydrocinnamyl alcohol, is the next higher homologue, and is found in storax and in cassia oil. It yields a phenyl-urethane melting at 47–49°, and has a rose-like odour which is of value in the preparation of modifications of rose odours. It has the following characters:

Sp. gr. at 15.5°.................................... 1.007
B. p. ................................................ 235°
Opt. rot. ........................................... 0°

### Cinnamic Alcohol

This alcohol, of the constitution $C_6H_5.CH:CH.CH_2OH$, is of fairly common occurrence in storax, balsam of Peru and other

balsamic substances, and also in the essential oil of hyacinths. It occurs both in the free state and in the form of esters. It is crystalline, melting at 33°, but owing to traces of impurities, commercial specimens are usually liquid at 20° or thereabouts. Pure cinnamic alcohol has the following characters:

M. p. ........................................ 33°
B. p. at 760 mm. .............................. 258°
Sp. gr. at 35° ............................... about 1.020
Ref. index at 20° ............................. 1.0302

Commercial specimens usually have a sp. gr. varying between 1.010 and 1.030 at 15.5°. Cinnamic alcohol forms a phenyl-urethane melting at 91° and a diphenyl-urethane melting at 97°–98°.

The odour recalls that of roses and hyacinths, in both of which types of perfume it is a useful adjunct.

### Perillic Alcohol

This alcohol, of the formula $C_{10}H_{16}O$, was first isolated from gingergrass oil by Schimmel & Co. It is also obtained by the reduction of perillic aldehyde, $C_{10}H_{14}O$, a substance found in the essential oil of *Perilla Nankinensis*. Perillic alcohol has the following characters:

B. p. ................................... 119–121° at 11 mm.
Sp. gr. at 15.5°......................... 0.969 at 20°
Ref. index at 20° ....................... 1.4996
Sp. rot. ................................ −68.5°

It yields perillic aldehyde on oxidation, and this substance forms a semicarbazone melting at 130°–131°, and a naphthyl-urethane melting at 146° to 147°.

### (3) CYCLIC TERPENE ALCOHOLS

#### Borneol, Bornyl Alcohol, $C_{10}H_{17}OH$

Borneol is one of the series of naturally occurring alcohols belonging to what is conveniently described as the "camphor series." These alcohols have, in most cases, corresponding ketones which occur naturally, so that they are mostly secondary alcohols. The following are the principal members of the series.

| Alcohol | Ketone |
|---|---|
| Borneol. | Camphor. |
| *Iso*borneol. | |
| Fenchyl alcohol. | Fenchone. |
| Thujyl alcohol. | Thujone. |
| Terpineol. | |
| Pulegol. | Pulegone. |
| Menthol. | Menthone. |

Borneol occurs as dextro-borneol in the wood of *Dryobalanops camphora* (Borneo camphor) and as lævo-borneol in *Blumea balsamifera* (Ngai camphor). It probably occurs also in the optically inactive variety, and in the essential oil of Virginian snake-root (*Aristolochia serpentaria*).

Borneol forms the main constituent of "*Borneo camphor.*" This, as imported, contains from 2 to 3.5% of resin and other impurities, from which the borneol can be separated by sublimation. Borneol may also be obtained by the action of sodium or of alcoholic potassium hydroxide on common camphor.

Borneol forms regular crystals which are lighter than water. It has an odour like that of camphor and a pungent peppery taste. Borneol melts at 204° and boils at 212°; but it sublimes readily below its m. p. and condenses in hexagonal plates.

Borneol is very sparingly soluble in water, but soluble in alcohol, ether, and petroleum spirit.

Natural borneol has a specific rotation of about ±37°. Borneol is present in the oils of lavender, rosemary, spike, etc. The fusel oil of the spirit obtained by the fermentation of the sugar of madder contains *l*-borneol, which is said by Haller also to occur in the forms of acetate, formate, and valerate in the oil of valerian.

According to Haller, a racemoid modification of borneol, consisting of a mixture of dextro- and lævo-borneols in equal proportions, is obtained by the distillation of the crude "terebene" resulting from the action of sulphuric acid on turpentine oil.

An optically inactive borneol, m. p. 199°, was obtained from colophony by Armstrong and Fielden.

Borneol forms a series of esters of which several are to be found in various essential oils. The following are the characters of the principal of these esters:

|  | B. p. | Sp. rot. | Sp. gr. at 15.5° | Ref. index at 15° |
|---|---|---|---|---|
| Formate............... | 90° | +31° | 1.013 | 1.47078 |
| Acetate............... | 98° | −38° 20′ | 0.991 | 1.46635 |
| Propionate............. | 110° | +24° | 0.978 | 1.46435 |
| Butyrate.............. | 121° | +22° | 0.966 | 1.46380 |
| Valerate.............. | 128–130° | +20° | 0.956 | 1.46280 |

Borneol forms a phenyl-urethane, m. p. 138°. It also forms crystalline compounds with chloral and bromal, the former melting at 55°, and the latter at 105°. It forms an acid phthalate melting at 164°.

Bredt considers that borneol is stereoisomeric with *isoborneol* (*q.v.*), the OH group being turned away from the ring in borneol, and toward the centre in *iso*borneol. He thus terms borneol *exo*borneol, and *iso*borneol *endo*borneol.

**Isoborneol.**—The borneol obtained by the reduction of camphor is stated to contain an admixture of a modification known as *isoborneol*, which is also obtained by warming camphene with acetic acid and a little sulphuric acid, and decomposing the acetate formed by alcoholic potassium hydroxide. This reaction is employed by Bertram and Walbaum (*J. pr. Chem.*, 1894, [2], **49,** 15) for the detection of camphene in the oils of lemon, ginger, etc.

*Iso*borneol agrees with the ordinary modification in yielding camphor, etc., on oxidation by dilute nitric acid.

The characters of the two substances are compared in the following table:

|  | Borneol | Isoborneol |
|---|---|---|
| Crystalline form.................... | Hexagonal | Hexagonal laminæ |
| M. p............................. | 204° | 212° |
| B. p............................. | 212° | ................ |
| Solubility in benzene, at 0°........... | 1 : 7 | 1 : 3 |
| Solubility in petroleum spirit at 0°..... | 1 : 10 | 1 : 4 |
| M. p. of chloral compound........... | 55 to 56° | liquid |
| M. p. of bromal compound........... | 105° | 71 to 72° |
| Acetate........................... | 29° | liquid |
| Acetate; b. p. at 15 mm. pressure, °.... | 106 to 107 | 107 |
| Sp. rot........................... | 37° | 34° |

Dehydrating agents convert isoborneol into *camphene*, whereas borneol is unaffected. *Iso*borneol is converted into the correspond-

ing ether when boiled with sulphuric acid and methyl or ethyl alcohol, whereas borneol does not yield ethers by this treatment.[1]

L. A. Tschougaef (*Bull. Soc. Chem.*, 1901, **26**, 298) purifies borneol from *iso*borneol by converting the alcoholate of borneol into methyl bornyl-xanthate, when steam-distillation removes the *iso*borneol. When heated with alcoholic potassium hydroxide and the liquid acidified the methyl ester yields borneol. According to Bredt, the formulæ for borneol and its ketone, camphor, are as follows:

<div style="text-align:center">

Borneol

CH$_2$—CH—CH$_2$
        |
       CMe$_2$        |
        |
CH$_2$—CMe—CH.OH

Camphor

CH$_2$—CH—CH$_2$
        |
       CMe$_2$        |
        |
CH$_2$—CMe—CO

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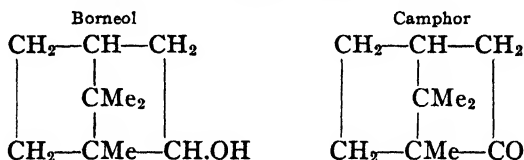
Henderson and Heilbron (*Proc. Chem. Soc.*, 1913, **29**, 381) recommend the following method for discriminating between borneol and isoborneol. The substance is dissolved in about 12 times its weight of pyridine, the calculated amount of *para*-nitrobenzoyl chloride added, and the mixture heated on a water bath for several hours. The pyridine is extracted with dilute H$_2$SO$_4$ at 0°, and the resulting *para*-nitrobenzoate of the alcohol is separated, dried and recrystallised from alcohol. The borneol compound melts at 137°, and the isoborneol compound at 129°. The melting points for borneol and isoborneol given above may require revision, as Henderson and Heilbron find that these figures determined on the alcohols regenerated from their *para*-nitrobenzoates are 208° for borneol and 217° for isoborneol.

### Fenchyl Alcohol, C$_{10}$H$_{17}$OH

Fenchyl alcohol rarely occurs naturally, but is easily obtained by the reduction of fenchone, its ketone, which is to be found in oil of fennel and oil of thuja. It is prepared by the reduction of the ketone, and 45°.

Naturally occurring fenchyl alcohol is an optically inactive solid crystalline substance m. p. at 33° to 35°. Wallach found the optically active varieties to each melt at 45°, but a mixture in equal parts

[1] According to F. W. Semmler (*Ber.*, 1900, **33**, 774), isoborneol on being heated with zinc-dust at 220° yields, as the chief product, *isodihydro-camphene*, C$_{10}$H$_{16}$, melting at 85°; whereas borneol remains unchanged when similarly treated. Since zinc is capable of removing oxygen from tertiary alcohols only (abst. *J. C. S.*, 1894, **1**, 611), the view that borneol and *iso*borneol are physical isomerides is untenable, the former being a secondary and the latter a tertiary alcohol.

melted at 33°–35°. The characters of the alcohol, prepared from fenchone are as follows:

B. p. ............................................... 201°
Sp. gr. at 50° ...................................... 0.933
M. p.... ........................................... 45°
Sp. rot............................................. ±15° 31′

Pickard, Lewcock and Gates (*J. Chem. Soc.*, 1913, **29**, 127) have prepared a fenchyl alcohol by reduction of *d*-fenchone. Although it was lævorotatory it was probably a mixture of the two optical varieties. By fractional crystallisation of the cinchonine salt of the acid phthalate, a separation was effected and the pure lævorotatory substance obtained.

Fenchyl alcohol yields a phenyl-urethane, m. p. 88° (from the inactive variety) or 82.5° (from the active variety). It also yields an acid phthalic ester, m. p. 145°. The terpene fenchone can be hydrated by treatment with sulphuric and acetic acids, and on hydrolysis of the resulting ester *iso*fenchyl alcohol is obtained, m. p.62°. This substance is related to fenchyl alcohol in the same way as *iso*borneol to borneol.

## Thujyl Alcohol, $C_{10}H_{17}OH$

Thujyl alcohol has been found occurring naturally in the essential oils of thuja leaves and wormwood leaves. It also results by the reduction of the corresponding ketone, thujone, by means of alcohol and sodium. It was originally described by Semmler under the name tanacetyl alcohol. It has the following characters:

B. p. at 760 mm. ................................. 210°–212°
B. p. at 13 mm. .................................. 92°–93°
Sp. gr. at 20° .................................... 0.925
Ref. index at 15.5°............................... 1.4635

An isothujyl alcohol also exists which Paolini (*Atti R. Accad. dei Lincei* v **20**, i, 765) has isolated from the reduction products of thujone. This isomer has the following characters:

B. p. ............................................. 206°
Sp. gr. at 15.5°.................................. 0.923
Ref. index at 20° ................................ 1.4617
Sp. rot........................................... +116.9°

Thujyl alcohol can be identified by oxidation with chromic acid, when thujone results; this substance forms an oxime melting at 54°.

## Terpineol, $C_{10}H_{17}.OH$

Terpineol of commerce is a colourless, strongly refractive, optically inactive liquid having the following characters:

|                        |                   |
|------------------------|-------------------|
| Sp. gr. at 15.5°       | 0.933 to 0.941    |
| B. p.                  | 217° to 220°      |
| Ref. index at 20°      | 1.4800–1.4840     |
| Opt. rot.              | ±0°               |

It has a very fragrant ódour of hyacinth or lilac-flowers, especially when diluted. By cooling to −50° terpineol yields crystals, m. p. 34° to 35°. Contact with these causes the solidification of terpineol at the ordinary temperature. Terpineol is not attacked by alkalies or fatty acids, and owing to this fact and its high b. p. (218° to 219°), it is extensively employed for scenting toilet soaps.

Terpineol is practically insoluble in water, but dissolves readily in alcohol, ether, hydrocarbons, and fatty oils.

Terpineol is an alcohol the constitution of which has long puzzled chemists. It is now known that there are at least 3 isomeric terpineols of which two at least are present in the terpineol of commerce. A study of the constitution of this alcohol shows that 12 stereo- and other isomers are possible.

The predominating isomer in the commercial variety is $\alpha$-terpineol.

Wallach originally prepared a terpineol by acting on terpin hydrate with phosphoric acid. His terpineol boiled at 215° to 218°, and was liquid. By using sulphuric acid, Bouchardat prepared it from terpin hydrate as a solid, m. p. 30° to 32°. Wallach has since shown that this solid variety really melts at 35°. Liquid terpineol of commerce appears to consist of the liquid variety, and of 2 solid isomers, one melting at 35° and the other at 32° to 33°. Semmler has recently prepared optically active terpineols (the ordinary varieties are inactive) by replacing the chlorine in the isomeric limonene hydrochloride by a hydroxyl group. The resulting terpineol is active in the same sense as the limonene from which it is prepared.

Bayer has also synthesised a terpineol, m. p. at 69°.

Terpineol m. p. at 32° ($\beta$-terpineol) has a sp. gr. of 0.923. It boils at 210° at normal pressure. Its phenyl-urethane m. p. at 85°. Terpineol, m. p. at 35° to 36°, has a sp. gr. 0.939, and b. p. 219°. Its phenyl-urethane m. p. at 112.°

Terpineol occurs naturally in several essential oils.

The liquid terpineol of commerce manufactured from terpin hydrate by the action of dilute sulphuric acid consists of a mixture of α-terpineol, m. p. 35°, which predominates, and of β-terpineol m. p. 32° and of liquid terpineol (*Wallach, Liebig's Annalen*, 1907, **356**, 218; 1908, **362**, 342) m. p. −1°. The terpineol melting at 69–70° has been termed γ-terpineol. The three varieties have the following characters:

| | α | β | γ |
|---|---|---|---|
| M. p. | 35°–38° | 32°–33° | 69°–70° |
| Sp. gr. at 15.5°. | 0.935–0.940 | 0.923 | ............... |
| Rotation | up to −117° | ............... | ............... |
| Ref. index at 20°. | 1.4810–1.4827 | 1.4747 | ............... |
| B. p. | 217–219° | 210° | ............... |

The probable constitutions of the 3 principal isomeric terpineols are as follows:

CH₃ CH₂

CH

H₂C  CH₂

H₂C  CH₂

C.OH

CH₃

M. p. 32–33°

(or)

CH₃ CH₃

COH

CH

H₂C  CH₂

H₂C  CH₂

C

‖

CH₂

CH₃ CH₃

COH

CH

H₂C  CH₂

HC  CH₂

C

CH₃

M. p. 35–36°

CH₃

COH

H₂C  CH₂

H₂C  CH₂

C

‖

C

CH₃ CH₃

M. p. 69–70°
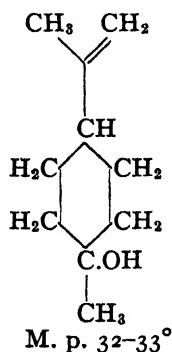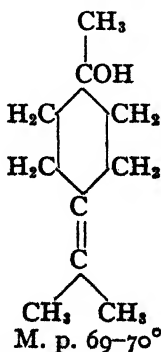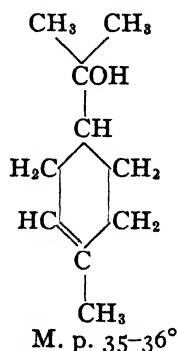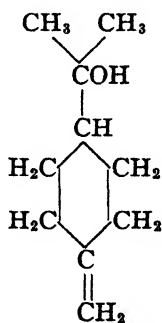
## Pulegol, $C_{10}H_{17}OH$ (and Isopulegol)

Pulegol, is a compound not occurring in nature, but which is obtained by the reduction of the natural ketone, pulegone. It is a viscous liquid, having an odour resembling that of terpineol, of sp. gr. 0.912 and b. p. 215°. It has never been separated in a state of absolute purity, so that its characters are not well defined. An isomer, *iso*pulegol, is formed by the treatment of citronellol with acetic anhydride. This alcohol, corresponding with the ketone *iso*-pulegone, has a sp. gr. 0.915, and a ref. index 1.4729. It is optically active, $[\alpha]_D$ —2.65°, and b. p. 91° at 13 mm.

The corresponding ketones are of more practical interest than the alcohols.

## Menthol, Menthyl Alcohol, $C_{10}H_{19}.OH$

Menthol has the constitution of a methyl-isopropyl-phenol hexa-hydride:

$$CH_3.CH\begin{cases} .CH_2.CH_2 \\ .CH_2.CH(OH) \end{cases} CH.CH.(CH_3)_2.$$
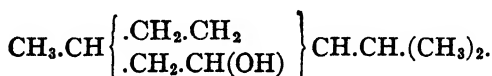
Menthol occurs, together with menthone and the hydrocarbon menthene, in peppermint oil, and separates in crystals on cooling the oil. The menthol from American oil of peppermint (derived from *Mentha piperita*) usually forms snow-white acicular crystals, or stellate groups of white satiny needles, having the characteristic odour and flavour of peppermint. The product from the Japanese and Chinese oils forms prismatic crystals closely resembling those of magnesium sulphate.

Pure menthol volatilises slowly at the ordinary temperature, m. p. 42° to 43°, and b. p. 215.5° (Power). Schimmel & Co. give the m. p. as 43.5°–44.5°. E. J. Parry gives the b. p. of menthol as 215°, and the sp. gr. as 0.881 at 45°.

Menthol is but slightly soluble in water, but imparts to the liquid its characteristic taste and smell. It dissolves readily in alcohol, ether,[1] carbon disulphide, and in fixed and volatile oils. The solutions are lævorotatory; $[a]_D$ = about —50°.

Menthol is not soluble in aqueous alkalies, a character which distinguishes it and permits of its ready separation from thymol and phenol.

[1] Waste or impure menthol may be purified by recrystallisation from its solution in ether, benzene, light petroleum, carbon disulphide, or acetone. When ether is employed as the solvent, the menthol crystals can be freed from all foreign odour by a few hours' exposure to the air. (A. W. Gerrard, *Pharm. J.*, 1909, 65, 163.)

The proportion of menthol contained in oil of peppermint, etc., is best ascertained by converting it into its acetic ester, as described later.

Menthol is extensively employed as a remedy for neuralgic headache and other affections. It forms the active constituent of the "neuralgic erystals," which, however, are liable to considerable adulteration. Thus, in addition to a legitimate economisation of the menthol by forming the base of the pencil of paraffin-wax, the menthol itself is sometimes mixed with paraffin; and fatty matters, thymol, and other substances have also been added (*Pharm. J.*, [3], **15,** 365, 686). To ascertain the quality of a pencil, a portion of the substance should be scraped from the surface and its m. p. determined. The commercial article fuses at 41° to 43°. An admixture of paraffin-wax notably raises the m. p. unless some other adulterant is also present. On heating a weighed portion of the exterior of the pencil to 100° the menthol will volatilise, and its quantity may be ascertained from the loss in weight, none of the probable admixtures, such as fatty matters, spermaceti, paraffin-wax, salicin, salicylic acid, thymol, etc., being sensibly volatile at 100°. Mineral matters, such as magnesium sulphate, which is said to have been used as an adulterant of menthol, will remain on heating the sample to dull redness in the air.

The ready solubility of menthol in cold 90% alcohol is a test of some value, as many adulterants (*e. g.*, paraffin, spermaceti, and fats) are insoluble in that solvent. The alcohol should be heated to boiling to ensure the complete solution of the menthol, and the liquid then allowed to cool. By operating in this manner the test may be made quantitative.

By reaction with acids, menthol readily yields *esters* and by treatment with phosphorus pentachloride or hydrochloric acid it is converted into *menthyl chloride*, $C_{10}H_{19}Cl$. By distillation with zinc chloride or phosphoric anhydride, menthol is converted into the hydrocarbon *menthene*, $C_{10}H_{18}$, a dextrorotatory liquid which has an odour of cymene, boils at 167°, and combines with bromine to form the addition-product $C_{10}H_{18}Br_4$. This is converted into *cymene*, $C_{10}H_{14}$, by heating and distilling the product with sodium.

Careful oxidation converts menthol into its ketone, menthone. The principal ester is menthyl acetate, a liquid which boils at 224°, and occurs naturally in oil of peppermint.

The reduction of menthone produces a mixture of dextro- and lævo-menthol having an optical rotation of $+2°$.

It will be convenient to discuss here, before passing on to the sesquiterpene alcohols, the indifferent substance cineol, which is an oxygenated compound, in which the oxygen does not enter into alcoholic, aldehydic or ketonic functions.

Commercial menthol, no doubt consists of substantially one chemical individual, but there are various isomers of menthol, which may be present in certain oils and so modify the particular "peppermint odour." F. E. Wright (*J. Amer. Chem. Soc.*, **39**, 1515) has made an exhaustive study of this question. He states that menthol crystallises in four different forms, which he term $a$, $b$, $c$ and $d$. Of these $a$ appears to be the stable form, and melts at $42.5°$; $b$ melts at $35.5°$, $c$ at $33.5$ and $d$ at $31.5°$. But the three latter forms invert to the stable form $a$ on standing. This work is however, unconvincing, and the questions of superfusion and traces of impurities may account for some of the author's observations.

The recent work of Pickard and Littlebury (*J. Chem. Soc.*, **101**, 109) is of great importance. Starting from the alcoholic mixture obtained by Brunel (*Comptes rendus*, **137**, 1288) by the reduction of thymol (which he had termed thymo-menthol), they separated it into a mixture of about 60% isomeric menthols, and 40% of menthones and other compounds. By means of a series of fractional crystallisations of the magnesium salts of the phthalic acid esters, they succeeded in separating the alcohols into at least two separate chemical individuals. Of these one was an inactive menthol melting at $34°$, and the other was a substance termed neomenthol melting at $51°$. These two substances had the following characters:

|  | MENTHOL | NEO-MENTHOL |
|---|---|---|
| M. p. | $34°$ | $51°$ |
| B. p. at 16 mm. | $103°–105°$ | $103°–105°$ |
| M. p. of phthalic ester | $129°–131°$ | $175°–177°$ |
| M. p. of phenyl-urethane | ......... | $114°$ |
| M. p. of succinic ester | ......... | $67°–68°$ |

Whilst it is probable that natural *lævo*- menthol is a chemical individual, it is possible that it occurs associated with these isomers in traces which modify the characters of commercial isolated specimens of ordinary menthol.

## Sabinol, $C_{10}H_{15}.OH$

This substance is a secondary alcohol, found in the essential oils of savin, eucalyptus and cypress. The purest specimen obtained by Paolini and Rebern (*Atti. R. Accad. dei Lincei*, 1916 (v) **25**, ii 377) had the following characters:

B. p. ...................................... 208°
Sp. gr. at 15.5°. ............................ 0.952
Ref. index at 20° ........................... 1.4895 at 18°
Sp. rot. .................................... +7° 56'

## Terpin Hydrate, $C_{10}H_{18}(OH)_2 + H_2O$

Terpin hydrate is of some commercial importance as it is used to a small extent in medicine. It is a crystalline alcohol prepared by the action of dilute mineral acids on various terpenes especially pinene and limonene. The following is a typical method for its preparation: a mixture of 8 parts of turpentine oil, 2 parts of alcohol, and 2 parts of $HNO_3$ (sp. gr. 1.255) is allowed to stand with occasional shaking for several days in a flat basin. The liquid is then poured from the first crop of crystals and neutralised, when a second crop will separate. Terpin hydrate forms well defined monoclinic prisms melting at 116°–117°.

## Teresantabol, $C_{10}H_{16}O$

This alcohol, of the formula $C_{10}H_{16}O$ was isolated from oil of sandalwood by Schimmel and Co. It has also been prepared artificially by Semmler and Bartelt (*Ber.*, 1907, 3321) by reducing teresantalic acid with sodium. It is a crystalline substance melting at 112–114° and forms a phthalic acid compound, m. p. 140°.

## Myrtenol, $C_{10}H_{16}O$

Myrtenol is a primary cyclic alcohol, found as its acetic ester in essential oil of myrtle. It forms an acid phthalate, m. p. at 116°, which is useful in separating it from geraniol, with which it occurs. It possesses an odour of myrtle, and has the following characters:

B. p. at 760 mm. ............................. 222°–224°
B. p. at 9 mm. .............................. 102°–105°
Sp. gr. at 20° .............................. 0.9763
Opt. rot. .................................. +45° 45'
Ref. index at 20° ........................... 1.4967

On oxidation with chromic acid it yields the corresponding alde-hyde, myrtenal, a liquid of sp. gr. 0.990, and having a ref. index 1.5042 at 20°.

## Dihydrocarveol, $C_{10}H_{18}O$

Dihydrocarveol is a natural constituent of caraway oil and also results from the reduction of carvone. Its odour is agreeable, recalling that of caraway oil. Its characters are as follows:

B. p. .......................................... $224°-225°$
B. p. at 7 mm. ................................... $100°-102°$
Sp. gr. at 15.5° ................................... $0.937$
Opt. rot. ......................................... $-6°\ 14'$
Ref. index at 20° ................................. $11.4836$

It yields a phenyl-urethane m. p. 87° (optically active variety) or 93° (optically inactive variety).

## Santelol, $C_9H_{16}O$

This alcohol may be conveniently discussed here. It occurs in oil of sandalwood, and has also been termed santenone alcohol, or $\pi$-nor-borneol. Its characters are as follows:

B. p. ................................... $87°-88°$ at 9 mm.
M. p. ................................... $68°-70°$
Opt. rot. ............................... $0°$

It forms an acetate of sp. gr. 0.987, and ref. index 1.4596.

## Cineol (Eucalyptol), $C_{10}H_{18}O$

This compound exists to a very large extent in oils of eucalyptus, wormseed, cajuput, and spike lavender. It is also found to a lesser extent in other oils. It has been described under the names eucalyptol (its most common commercial name) and cajuputol.

Cineol is a product of the action of boiling phosphoric and other mineral acids on terpin hydrate, which is itself readily prepared from turpentine oil.

Cineol is a colourless liquid, having a characteristic camphoraceous odour, and a pungent cooling taste. The sp. gr. of liquid cineol at 15° is 0.930. When exposed to a low temperature, it solidifies to a mass of colourless needles, which melt at +1°. Cineol boils at 176° to 177°. Its ref. index is 1.4596, and it is optically inactive.

Cineol is soluble in all proportions in alcohol, glacial acetic acid, ether, chloroform, benzene, carbon disulphide, and fatty and volatile

oils. It is not dissolved by water nor by aqueous solutions of alkali hydroxides. Cineol is itself a solvent of caoutchouc, gutta-percha, benzoic and salicylic acids, phenol, etc.

Eucalyptol,[1] from the oil of *Eucalyptus globulus* or allied species, is now somewhat extensively employed in medicine, the internal dose ranging from 2 to 5 grains. In addition to the characters given above, the alcoholic solution of the commercial article should be neutral to litmus and should not develop a brownish or violet colour on the addition of a drop of tincture of ferric chloride. Such a reaction would indicate the presence of phenols, the amount of which can be ascertained by titrating the sample in alcoholic solution, with an equal measure of $N/2$ sodium hydroxide.

Cineol unites with bromine to form the compound $C_{10}H_{18}O$, $Br_2$, which crystallises in red needles and prisms.

When cineol is agitated with a strong solution of iodine in potassium iodide, a pasty mass is formed in which green lustrous crystals may be observed. These may be dried partially on a porous plate, but they rapidly deliquesce. The reaction may be employed for the detection of cineol.

By treatment with oxidising agents cineol is readily converted into *cineolic acid*, $C_{10}H_{16}O_5$.

Cineol does not react with phenylhydrazine or hydroxylamine, nor does it combine with bisulphites. When heated with alcoholic sulphuric acid, cineol yields terpinene and terpinolene.

From the foregoing characters it appears that cineol is neither a phenol, a ketone, an aldehyde, nor a true alcohol. The oxygen atom appears to be wholly indifferent. The constitution of cineol is probably that of cinyl oxide, $C_{10}H_{18}:O$, which bears the same relation to terpin that ethylene oxide bears to glycol.

Cineol forms a crystalline compound with iodol, of the formula $C_{10}H_{18}O.C_4I_4NH$, m. p. 112°. It also forms a crystalline compound with resorcinol.

The estimation of cineol or eucalyptol is a matter of considerable importance, as the valuation of eucalyptus oil (and to some extent other essential oils) depends entirely on the eucalyptol content. Early attempts in this direction were directed to the fractionation of

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[1] Eucalyptol may be conveniently prepared from such of the oils of eucalyptus as contain it by treatment with a strong solution of phosphoric acid (preferably of 1.785 sp. gr.), when a crystalline compound of the composition $C_{10}H_{18}O.H_3PO_4$ separates. This is separated and decomposed by hot water, when the liberated eucalyptol separates as an oily layer, which, after washing by agitation with water, is practically pure. (L. R. Scammel, Brit. Patent, 1894, No. 14138.)

the oil, and the subsequent freezing out of the eucalyptol.    But such methods gave but very approximate results and are not now used. No process can be said to give absolutely accurate results, so that it is necessary to state the process used in comparing results obtained by different observers.

The most generally adopted method for the estimation of eucalyptol is based on the observation of L. Scammel that phosphoric acid forms a crystalline compound with it.    It has usually been assumed that the compound in question was one in simple molecular proportions, and that it invariably had a definite composition, and Helbing and Passmore (*Pharmacological Record,* xxxv) described a method based on the weight of the eucalyptol phosphate obtained, assuming that each 100 parts of the phosphate contained 61.1% of eucalyptol.    Baker and Smith, however (*Research on the Eucalypts 2d edition,* 1920, 359) show that such an assumption cannot be accepted in practice, as the composition of the crystalline compound is variable, and give the average eucalyptol value as 59.5%.

Approximate results may be obtained by the following method. To about 5 grm. of the oil, 1 to 1.5 times its weight of phosphoric acid (sp. gr. 1.750) is added, drop by drop, with constant stirring. the mixture being kept cold during the process.    The acid should be added until the oil is semi-solid and commences, as a rule, to turn a deep brick red colour.    The crystalline magma is at once pressed between porous paper, in, for example, a copying press, until the porous paper absorbs no more liquid.    Several changes of paper are necessary and under the best conditions a little uncombined terpenes, etc., will be retained by the eucalyptol phosphate.    The crystals are then decomposed by warm water in a flask with a graduated neck, and the eucalyptol measured.    Its sp. gr. may be taken as 0.930 from which its weight is calculated.    If the oil be first diluted with about half its volume of petroleum spirit the results are more accurate.    This process is not of any value when the eucalyptol content is much below 40%.    Baker and Smith (*loc. cit.*) give the following process which they claim yields fairly accurate results with oils containing 20% or over of eucalyptol.    If a preliminary test indicates over 60% of eucalyptol, the oil is first diluted with one-third its volume of freshly distilled pinene (or turpentine oil). Ten c.c. of the oil are mixed with 4 c.c. of glacial phosphoric acid, added drop by drop, with continual stirring, the mixture being kept

in an ice bath. If the oil contains less than 30% of eucalyptol, only 3 c.c. of phosphoric acid are necessary. The mixture is allowed to stand in the ice bath for 5 to 10 minutes. Ten c.c. of ice cold petroleum spirit (b. p. below 59°) are then added to the magma and incorporated with it by means of a flat-headed glass rod. The mixture is then rapidly filtered by means of a filter pump, and the cake of crystals strongly pressed between calico and filter paper, decomposed with hot water and the eucalyptol measured.

Schimmel & Co. have recommended absorbing the eucalyptol by means of a 40–50% solution of resorcin, and reading the unabsorbed portion in the graduated neck of the flask. But as resorcin absorbs many oxygenated constituents, the results obtained are necessarily inaccurate where more than traces of oxygenated constituents other than eucalyptol are present. To somewhat obviate this difficulty, the determination may be carried out on the fraction of the oil boiling between 170°–190°, but even then the results are not satisfactory. Dodge (*J. Ind. Eng. Chem.*, 1912, 4, 592) has published a method depending on the oxidation of the terpenes by means of potassium permanganate, but this method does not yield accurate results. Turner and Holmes (*Perfumery and Essential Oil Record*, 1915, 21) suggest the following process, which is fairly satisfactory. Ten c.c. of the oil are delivered by a pipette into a round bottomed glass dish packed in ice. Ten c.c. of 85% arsenic acid are gradually added with constant stirring. When no further solidification takes place, the mixture is left on the ice for 10 minutes, and if the mass is hard, the oil is known to be rich in eucalyptol. Five c.c. of petroleum spirit are then added, and the well mixed mass transferred to hardened filter paper and well wrapped up in absorbent filter paper. The mass is pressed in a copying press, and the paper changed until the mass is dry. The arsenate is then decomposed by warm water and the eucalyptol measured as usual. With oils containing less than 45% of eucalyptol this method is inapplicable.

T. T. Cocking (*Perfumery and Essential Oil Record*, 1920, 281) has described the latest method for this estimation which yields very good results. Belluci and Grassi (*Chem. Zentral.*, 1914, 1, 884) have shown that eucalyptol combines in equimolecular proportions with other phenols than resorcinol and prepared the following substances:

| With | M. P. |
|------|-------|
| Phenol... ........................................ | +8° |
| Ortho-cresol........................................ | +50° |
| Meta-cresol......................................... | −5° |
| Para-cresol......................................... | +1.5° |
| Pyrocatechol........................................ | +39° |
| Resorcinol.......................................... | −15° |
| Thymol............................................. | +4.5° |

Cocking's method consists in the determination of the freezing point of a mixture of eucalyptus oil and cresol in quantities proportional to the molecular weights of eucalyptol and cresol. A stout walled test tube about 15 mm. in diameter and 80 mm. in length, fitted with a bent wire loop for suspending from the balance, is so suspended, and exactly 3 grm. of the oil and 2.1 grm. of melted *ortho*-cresol are weighed into it. The tube is then inserted through a bored cork in a small wide mouthed bottle to act as an air bath, and the mixture stirred with a thermometer and the freezing point noted. The mixture is then warmed and well mixed and the freezing point noted until concordant results are obtained. The first figure noted is usually several degrees higher than the late concordant figures. This is due to the rapid crystallisation taking place before the substances are completely mixed. Where the amount of eucalyptol is low, the mixture must be sown with a crystal of the compound, which has been named cresinol, in order to induce solidification. Under the above conditions, it is claimed that by taking the means of several observations, the error lies between ±3%. The following are determined values, from which, by interpolation, intermediate values may be calculated:

| % of Eucalyptol | Freezing Points (Terpene mixture) | Freezing Point (Sesquiterpene mixture) |
|-----------------|-----------------------------------|----------------------------------------|
| 100 | 55.2° | 55.2° |
| 95 | 53.4° | 53.6° |
| 90 | 51.2° | 51.7° |
| 85 | 48.5° | 49.7° |
| 80 | 45.8° | 47.7° |
| 75 | 43.2° | 45.7° |
| 70 | 40.6° | 43.8° |
| 65 | 37.4° | 41.2° |
| 60 | 34.2° | 37.4° |
| 55 | 29° | 33.6° |
| 50 | 25.4° | 29.8° |
| 45 | 22.2° | 26.2° |

### Sesquiterpene Alcohols

A number of sesquiterpene (or closely allied) alcohols of the formula $C_{15}H_{23}OH$ (or $C_{15}H_{23}OH$) occur in various essential oils,

usually those having a high boiling point. They are frequently solid crystalline compounds, hence they have often been described as "camphors," a name now obsolete as applied to such substances. They are closely related to the sesquiterpenes, and in many cases are converted into the corresponding hydrocarbons by dehydration. Caryophyllene alcohol, an alcohol corresponding with the sesquiterpene caryophyllene, however, is an exception; since, although it is prepared from caryophyllene, it yields a different sesquiterpene, clovene, on dehydration.

A few of the more important of these will be described, less important members of the group being dealt with in tabular form.

### Santalol, $C_{15}H_{24}O$

Santalol is the main constituent of sandalwood oil, and is extracted therefrom and forms a regular commercial article. It is a mixture of at least two primary unsaturated alcohols termed $\alpha$-santalol and $\beta$-santalol.

The following are the average characters for commercial santalol:

Sp. gr. at $15.5°$ .......................... $0.973$ to $0.979$
Opt. rot. .................................... $-14°$ to $-24°$
Ref. index at $20°$ .......................... $1.5040$ to $1.5090$
Total alcohols, $C_{15}H_{24}O$. ..................... $98-100\%$

Paolini and Divizia (*Atti. R. Accad. Lincei*, 1914, v, **28**, ii, 226) have separated the isomers by fractionating as far as possible, converting the fractions into the hydrogen phthalates, and these into their strychnine salts, and repeatedly fractionating the crystals until melting points and rotations are constant. The characters of the two isomers are approximately as follows:

|  | $\alpha$-SANTALOL | $\beta$-SANTALOL |
|---|---|---|
| B. p. at 760 mm............... | $300°-301°$ | $309°-310°$ |
| B. p. at 760 mm............... | $155°$ at 8 mm. | $168°-169°$ at 10 mm. |
| Sp. gr. at $15.5°$.............. | $0.979$ | $0.9729$ |
| Ref. index at $20°$............... | $1.4990$ at $19°$ | $1.5092$ |
| Sp. rot...................... | $+1° 6'$ | $-42°$ |

The so-called West Australian sandalwood oil is not a true sandalwood oil, but is distilled from a tree called *Fusanus spicatus*. It is customary, however, to give the percentage of alcohols present in the oil, calculated as "santalol." Rao and Sadobrough (*J. Ind. Inst. Sci.*, 1923, **5**, 163) have examined the constituents of this oil and state that there are two isomers of santalol present, which they

have named $\alpha$-fusanol and $\beta$-fusanol, $C_{15}H_{24}O$. They have the following characters:

|  | α-FUSANOL | β-FUSANOL |
|---|---|---|
| Sp. gr. at 15.5°................................ | 0.9775 | 0.9753 |
| Sp. rot...................................... | +5.7° | +26° |
| Ref. index at 25°.............................. | 1.5060 | 1.5100 |
| B. p. at 5 mm................................ | 146°–149° | 153°–155° |

### Cedrol, $C_{15}H_{26}O$

Cedrol is a true sesquiterpene alcohol, found in oil of cedarwood and allied essential oils. It is a crystalline substance m. p. 86°–87°, b. p. 291°–294° and having a specific rotation (in chloroform) +9° 31′. It yields a phenyl-urethane melting at 100°–107°. It is associated with an isomer, which has been named pseudo-cedrol, a liquid alcohol of sp. gr. 0.9964 at 15.5°. They are probably physical isomerides.

### Zingiberol, $C_{15}H_{26}O$

The fraction of ginger oil boiling at 154°–157° at 15 mm. consists mainly of a sesquiterpene alcohol, zingiberol. It has a fragrant odour of ginger and yields zingiberene on dehydration.

### Guaiol, $C_{15}H_{26}O$

This sesquiterpene alcohol occurs in the so-called guaiac-wood oil, a useful perfume oil distilled from the wood of *Bulnesia Sarmienti*. It is a bi-cyclic tertiary alcohol, having the following characters:

| | |
|---|---|
| M. p........................................ | 91° |
| Ref. index at 20° ............................. | 1.5100 |
| Sp. rot...................................... | −29° |

### Eudesmol, $C_{15}H_{26}O$

Eudesmol occurs in numerous essential oils of the eucalyptus group. It has the following characters:

| | |
|---|---|
| M. p........................................ | 79°–80° |
| B. p. at 10 mm. ............................. | 156° |
| Sp. gr. at 20° ............................... | 0.9884 |
| Sp. rot. (in chloroform) ...................... | +38° to +43° |
| Ref. index at 20°............................. | 1.5160 |

It forms an acetate boiling at 165°–170° at 11 mm., and yields the sesquiterpene eudesmeme, on dehydration.

## Globulol, $C_{15}H_{26}O$

Globulol has been isolated from the essential oil of *Eucalyptus globulus*. It is a crystalline solid, m. p. 88.5°, and b. p. 283°. It yields two isomeric sesquiterpenes on dehydration. It is, probably, related to eudesmol in the same way as isoborneol is to borneol.

The following table embraces the other more commonly known sesquiterpene alcohols:

| Sesquiterpene | Source | Sp. gr. at 15.5° | Ref. index at 20° | M. p. | B. p. | Sp. rot. |
|---|---|---|---|---|---|---|
| Amyrol............. | West Indian sandalwood oil | 0.980 | ...... | ........ | 300° | +27° |
| Atractylol........... | Atractylis oil | .......... | 1.5103 | 59° | 290° | −17° |
| Betulol............. | Birch bud oil | 0.975 | 1.5018 | ........ | 288° | −35° |
| Cedrenol........... | Cedar wood oil | 1.0045 | 1.5230 | ........ | 161°–170° at 10 mm. | + 1° |
| Costol............. | Costus root oil | 0.987 | 1.5200 | ........ | 170° at 11 mm. | +13° |
| Cubeb camphor...... | Cubeb oil | .......... | ...... | 68°–70° | 248° | ........ |
| Elemol............. | Elemi oil | 0.944 | 1.5030 | ........ | 154° at 17 mm. | − 5° |
| Gonostylol.......... | Gonostylus oil | .......... | ...... | 82° | 165° at 17 mm. | +30° |
| Ledum camphor...... | Oil of Sedum palustre | 0.9814 at 20°/40° | 1.5072 | 104° | 281° | ........ |
| Machilol........... | Machilus oil | .......... | ...... | 79°–80° | 160° at 14 mm. | +30° |
| Matico camphor..... | Matico oil | .......... | ...... | 94° | .......... | −28.7° |
| Patchouli camphor... | Patchouli oil | .......... | ...... | 56° | .......... | −118° |
| Vetivenol.......... | Vetivert oil | 1.0245 | 1.5244 | ........ | 170°–174° at 13 mm. | +34° 30' |

## (C) PHENOLS AND PHENOLIC COMPOUNDS

A considerable number of substituted phenols occur as constituents of essential oils. Substitution by ethyl does not seem to occur naturally. In the case of the phenolic ethers of essential oils, the phenolic hydrogen appears to be almost invariably replaced by methyl.

As these substances have alcoholic functions in the phenolic OH group, as well as acidic functions, they may be conveniently studied here, before passing on to the aldehydes, ketones, esters, etc.

## Diphenyl Oxide

Diphenyl oxide $C_6H_5.O.C_6H_5$ is a substance of considerable importance as it forms the basis of most of the artificial geranium `oils of commerce. It forms long crystals, m. p. 27°–28°, and b. p. 253°. It is manufactured in large quantities, by, for example, di-

gesting diazo-benzene sulphate with phenol. Diphenyl-methane $C_6H_5.CH_2.C_6H_5$ is also used as an artificial geranium perfume. It is a crystalline substance, m. p. 26°–27° and b. p. 261°. Both compounds have a powerful geranium odour.

## Cresol Derivatives

*Para*-cresol and its methyl ether are present in certain flower oils and are of considerable importance in synthetic perfumery. *Para*-cresol is present in the oils of jasmin and cassie flowers. It is a crystalline substance, m. p. 36° and b. p. 199°. It can be identified by treating its alkaline solution with dimethyl sulphate, when its highly odorous methyl ether is formed, which on oxidation by potassium permaganate yields anisic acid, m. p. 180°. The methyl ether is found in ylang-ylang oil, and is prepared artificially as the basis of so called synthetic ylang-ylang oils. It is a liquid, b. p. 175°, and yielding anisic acid on oxidation.

These substances have the following constitutions:



*p*-cresol          *p*-cresol-methyl-ether
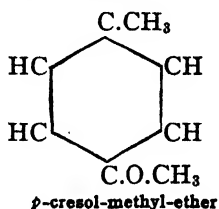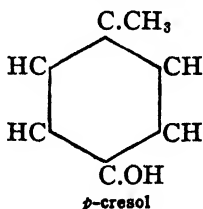
The other isomeric cresols are not of much importance in perfumery, but *meta*-cresol has been found in small quantity in the essential oil of myrrh. It is a crystalline substance, m. p. 4° and b. p. 201°. It forms a tribromide, m. p. 82°.

The estimation of the amounts of these substances present in a complex synthetic perfume is a practical impossibility except as a matter of lengthy research. The general character of such a mixture, which consists of esters, free alcohols, phenolic compounds and sometimes traces of such substances as indol and skatol, is readily recognised by the odour, and the constituents can be recognised qualitatively. The cresol compounds are most easily recognised by oxidation to the characteristic anisic acid.

## Methyl-propyl Phenols, Etc.

Several substances existing naturally in essential oils have the constitution of *methyl-isopropyl-phenols*. This structure may be

regarded as established in the case of thymol and carvacrol. The isomerism of carvacrol and thymol is exhibited by the following formulæ, whence it appears that they are both methyl-isopropyl-phenols.
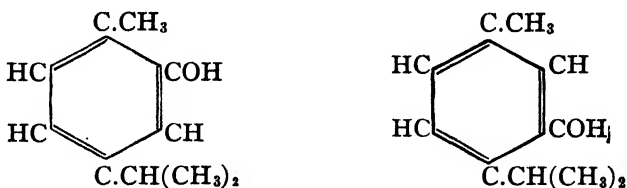


**Thymol, $C_{10}H_{13}OH$**

Thymol is the principal constituent of thyme oil, and is also contained in the volatile oils of horse-mint, wild-thyme, ajowan, etc. It may be extracted from thyme oil by agitation with a 5% solution of sodium hydroxide. The aqueous layer is separated and treated with excess of dilute acid, when the thymol rises to the surface as an oily layer. Another method of extraction is to expose the crude oil to a temperature of 0°, when the thymol crystallises out, and may be purified by recrystallisation from alcohol or glacial acetic acid. Naturally thymol is prepared from oils of thyme, ajowan, and similar oils rich in the phenol.

Thymol is prepared synthetically by treating dibromo-*p*-cymene with fuming sulphuric acid, and acting on the resulting dibromo-*p*-cymene-sulphonic acid with zinc dust and ammonia to eliminate the bromine. The product is then fused with potassium hydroxide, when the potassium thymolate obtained is decomposed by sulphuric acid, and the resulting thymol purified by crystallisation.

The artificial preparation of thymol is becoming a matter of considerable importance on account of the extended use of this phenol, which has considerable antiseptic and preservative properties.

Smith and Penfold (*J. and Proc. Royal Soc. N. S. W. Liv.*, **40**) have described its preparation from piperitone, the ketonic substance isolated by Smith from various eucalyptus oils. Sixty grm. of piperitone (*q. v.*) are added to a solution of 175 grm. of ferric chloride, 160 c.c. of glacial acetic acid and 500 c.c. of water. The whole was heated to boiling point for one hour. The reaction product was then steam distilled, the phenol separated and absorbed by 5% sodium hydroxide solution, the unabsorbed portion removed by ether, and

the aqueous solution decomposed by hydrochloric acid. The phenol was then distilled under reduced pressure, and a 25% yield of thymol was obtained.

The waste oil resulting from the sulphite pulping process on spruce wood is very rich in cymene, and numerous processes have been devised for the preparation of thymol from this product. The following is typical of such processes (Patent of Max Phillips, U. S. A.). The purified *para*-cymene is slowly added to an equal weight of sulphuric acid (sp. gr. 1.84), the mixture being kept at 0°. To this is slowly added cold nitrating mixture (1 part of nitric and 2 parts of sulphuric acid), the temperature being kept at 0° all the time. The mixture is stirred for an hour and then poured into cold water and the oily layer separated. This is washed with water, then with sodium carbonate solution and then again with water. The nitro-cymene thus obtained is converted into amino-cymene by reduction with iron and hydrochloric acid. The cymidine is then sulphonated, and the cymidine-sulphonic acid is diazotised in the usual manner by treating with sodium nitrite in acid solution. The diazo compound is reduced by alkaline stannous chloride. The amido group is thus eliminated and the appropriate cymenesulphonic acid results. The sodium salt is fused with sodium hydroxide, when thymol results.

McKee (U. S. Pat. No. 1,449, 121) produces a mixture of thymol and carvacrol by his process of sulphonation, etc., which he separates as follows. To the mixture is added 3 times its weight of well dried powdered lead actate and the mixture allowed to stand for 24 hours. The mass is broken up and washed with petroleum spirit. The thymol-lead acetate compound is insoluble in the petroleum spirit, whilst carvacrol and any carvacrol-lead acetate compound (which is formed with difficulty) are soluble, and are removed by the petroleum spirit. The thymol compound is washed with petroleum spirit and decomposed by steam, when thymol passes over. The carvacrol is similarly recovered from the residue of evaporation of the filtrate.

Thymol forms a methyl ether, which is found in the essential oil of *Crithmum maritimum*. It boils at 214°–216° and has a specific gravity of 0.954 at 0°.

Thymol is homologous with phenol and cresol, which it closely resembles in its general properties. It forms a series of crystallisable

salts, many of which distil unchanged. Thymol is a powerful antiseptic, its preservative power being considerably greater than that of phenol. It acts as a caustic on the lips and mucous membrane, but does not irritate the skin like carbolic acid.

Thymol forms large colourless crystalline plates having a feeble aromatic smell and burning, peppery taste. It melts, when pure, at 51° and does not readily resolidify unless touched by a solid substance or a crystal of thymol. It boils at about 232°. Solid thymol is slightly heavier than water (sp. gr. 1.028), but in the fused state it is rather lighter. In water, thymol is scarcely soluble, requiring about 1200 parts of cold or 900 of boiling water. Even this dilute solution is powerfully antiseptic. Rectified spirit dissolves its own weight of thymol, the greater part separating again on dilution with water. An alcoholic solution of thymol of about 1% strength is miscible with water in all proportions. Thymol is very sparingly soluble in glycerol, requiring 120 parts for solution. The thymol is precipitated by an equal volume of water, but is perfectly miscible with 4 volumes. The solution so obtained is a useful antiseptic lotion.

Thymol is readily soluble in glacial acetic acid. It is also freely dissolved by ether, chloroform, benzene, petroleum spirit, and oils. When thymol and camphor are triturated together, a syrupy liquid is obtained, which is readily miscible with vaseline and similar preparations. Thymol is insoluble in small quantities of alkaline liquids, but dissolves in presence of an equivalent amount of sodium hydroxide (40 of alkali to 150 thymol), forming a soluble crystallisable compound, $C_{10}H_{13}.ONa$, which is decomposed by acids with separation of the thymol.

Thymol is not dissolved by solution of ammonia, but it absorbs ammonia gas, with liquefaction, and resolidifies when the ammonia is allowed to escape by exposure to air.

When thymol is heated to 100° with strong sulphuric acid, it is converted into *thymol-p-sulphonic acid*. (A small quantity of thymol-disulphonic acid is simultaneously formed.) If the solution be diluted with 10 times its measure of water and the liquid digested with excess of white lead and filtered, the filtrate contains lead thymo-sulphonate and acquires a beautiful violet-blue colour on adding a drop of ferric chloride. Phenol gives a similar reaction.

With excess of bromine water, solutions of thymol yield a yellow-ish-white precipitate of a di-bromo-derivative.[1]

A delicate test for thymol consists in heating the solution with half its volume of glacial acetic acid, and at least its own volume of concentrated sulphuric acid, when a fine violet-red coloration will be produced, not destroyed by boiling, and having a characteristic absorption spectrum. J. F. Eykmann modifies this test by dis-solving a little of the sample in 1 c.c. of glacial acetic acid, and adding 5 or 6 drops of strong sulphuric acid and 1 drop of nitric acid, when, if thymol be present, at first a greenish and then a fine blue coloration will make its appearance in the lower part of the test-tube, and will spread throughout the liquid on shaking. Phenol gives a violet-red colour, but menthol, camphor, borneol, and salicylic acid give no colour-indication when similarly treated.

Tested with the reagents for phenol an aqueous solution of thymol gives the following indications:

Thymol gives no coloration with ferric chloride.

With ammonia and hypochlorites, strong solutions of thymol give a greenish colour, changing very slowly to blue-green and red, but with more dilute solutions a mere turbidity is produced on heating, without any colour resulting.

With sodium hypochlorite and aniline, thymol behaves like phenol.

Thymol in tolerably strong solutions (1 in 5000) gives a red or violet colouration or precipitate with Millon's reagent, but the reaction is far less delicate than with phenol, and the colour is destroyed by boiling.

Thymol reduces gold and platinum from their solutions (the latter only on boiling) far more readily than does phenol.

It appears from the above that *phenol* in presence of thymol may be best detected by its reaction with ferric chloride, and in very dilute solutions by ammonia and hypochlorite. In the concentrated state, thymol is distinguished from phenol by its less ready solubility in water, glycerin, and alkaline liquids, and by forming a liquid bromo-derivative. It may be separated from phenol by fractional distillation, and from *menthol* by treatment with excess of strong solution of sodium hydroxide.

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## Carvacrol, $C_{10}H_{13}OH$

Carvacrol, as mentioned above, is closely related to thymol. It occurs, often in association with thymol, in certain varieties of thyme and origanum oil. It results artificially by treating carvone with potash or with phosphoric acid, and also by fusing the appropriate cymene-sulphonic acid with caustic soda.

Carvacrol is a colourless liquid, of fragrant odour; having the following characters:

M. p.................................................... $1°$
B. p.................................................... $236°$
Sp. gr. at $15.5°$...................................... $0.981$
Ref. index at $20°$.................................... $1.5240$
Opt. rot............................................... $0°$

It yields a phenyl-urethane melting at $141°$.

## Creosol, $C_7H_8O_2$

Creosol is a phenol occurring in oil of ylang-ylang. It is an odoriferous oil, boiling at $220°$ and having the constitution .



## Thymohydroquinone, $C_{10}H_{14}O_2$

Thymohydroquinone and its dimethyl ether are found as constituents of a few essential oils, the former for example in those of *Callitris quadrifolia* and *Monarda fistulosa*, and the latter in that of arnica root. Thymohydroquinone is a crystalline compound melting at $143°$ and boiling at $290°$, and the dimethyl ether has the following characters:

B. p. .................................................. $248°–250°$
B. p. at 12 mm. ....................................... $118°$
Sp. gr. at $15.50°$.................................... $0.991$ at $20°$
Ref. index at $20°$.................................... $1.5134$

## Naphthol Ethers

$\beta$-Naphthol methyl and ethyl ethers are important commercial articles, and are much used in synthetic perfumery. The methyl

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Ref. index at $20°$................................ $1.5134$

## Naphthol Ethers

$\beta$-Naphthol methyl and ethyl ethers are important commercial articles, and are much used in synthetic perfumery. The methyl

ether is a crystalline substance m. p. 72° and b. p. 274°. It has a neroli odour and is known as yara-yara or nerolin. It is prepared by digesting β-naphthol-sodium with methyl iodide in alcohol.

The corresponding ethyl ether is known in commerce as bromelia (or, also, as nerolin). It melts at 37° and boils at 282°. These substances have the following constitutions, R representing the ethyl or methyl radicles:
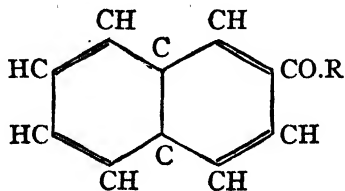


The corresponding butyl ether is sold as a fixative under the name fragarol.

## Allyl Phenols. Propenyl Phenols

A number of substances which exist in natural essential oils have the constitution either of allyl- or propenyl-phenols, or of methyl-esters of these compounds. Several compounds which contain the *allyl-group*, $CH_2:CH.CH_2—$, are convertible by molecular rearrangement into the corresponding compounds containing the isomeric *propenyl-group*, $CH_3.CH:CH—$. The transformation can usually be effected by boiling with alcoholic potassium hydroxide. Thus:

*Methyl-chavicol*, $CH_2:CH.CH_2.C_6H_4.OMe$,

yields *Anethol*, $CH_3.CH:CH.C_6H_4.OMe$.

*Safrol*, $CH_2:CH.CH_2.C_6H_3:O_2:CH_2$,

yields *Iso-safrol*, $CH_3.CH:CH.C_6H_3:O_2:CH_2$.

*Eugenol*, $CH_2:CH.CH_2.C_6H_3(OH).OMe$,

yields *Iso-eugenol*, $CH_3.CH:CH.C_6H_3(OH)OMe$.

*Apiol*, $CH_2:CH.CH_2.C_6H(OMe)_2:O_2:CH_2$,

yields *Iso-apiol*, $CH_3.CH:CH.C_6H(OMe)_2:O_2:CH_2$

The following are the principal members of this group of compounds, with their structural formulæ:

| Substance | Chief sources | Empirical formula | Constitutional formula |
|---|---|---|---|
| Chavicol (1–4-allyl-phenol)......... | Betel oil. Bay oil. | $C_9H_{10}O$ | $C_6H_3 \begin{cases} CH_2.CH:CH_2 \\ H \\ H \\ OH \end{cases}$ |
| Methyl-chavicol or estragol......... | Sweet basil oil. Bay oil. Chervil oil. | $C_{10}H_{12}O$ | $C_6H_3 \begin{cases} CH_2.CH:CH_2 \\ H \\ H \\ OCH_3 \end{cases}$ |
| Anethol......................... | Anise, star-anise and fennel oils, etc. | $C_{10}H_{12}O$ | $C_6H_3 \begin{cases} CH:CH.CH_3 \\ H \\ H \\ OCH_3 \end{cases}$ |
| Chavibetol (betel-phenol)........... | Betel oil. | $C_{10}H_{12}O_2$ | $C_6H_2 \begin{cases} CH_2.CH:CH_2 \\ H \\ OH \\ OCH_3 \end{cases}$ |
| Safrol.......................... | Sassafras, Japanese camphor and star-anise oils, etc. | $C_{10}H_{10}O_2$ | $C_6H_2 \begin{cases} CH_2.CH:CH_2 \\ H \\ O{>}CH_2 \\ O \end{cases}$ |
| Eugenol................. .... | Clove and cinnamon-leaf oils, etc. | $C_{10}H_{12}O_2$ | $C_6H_2 \begin{cases} CH_2.CH:CH_2 \\ H \\ OCH_3 \\ OH \end{cases}$ |
| Methyl-eugenol................... | Hazel-wort oil (*Asarum Europæum*), bay oil, etc. | $C_{11}H_{14}O_2$ | $C_6H_2 \begin{cases} CH_2.CH:CH_2 \\ H \\ OCH_3 \\ OCH_3 \end{cases}$ |
| Asarol (asarone) .................. | Hazel-wort oil, matico oil. | $C_{12}H_{16}O_3$ | $C_6H_2 \begin{cases} CH:CH.CH_3 \\ OCH_3 \\ OCH_3 \\ OCH_3 \end{cases}$ |
| Apiol (parsley-camphor)............ | Parsley oil. | $C_{12}H_{14}O_4$ | $C_6H \begin{cases} CH_2.CH:CH_2 \\ OCH_3 \\ OCH_3 \\ O{>}CH_2 \\ O \end{cases}$ |

## Chavicol, 1-4-Allylphenol, $C_3H_5C_6H_4.OH$

Chavicol forms from 30 to 40% of betel oil from fresh betel leaves, and is the constituent to which betel oil owes its pleasant, characteristic odour. It is also stated to be present, together with methyl-chavicol or estragol, in bay oil (*Myrcia acris*). Chavicol is a colourless oil, and but slightly soluble in ammonia. It has a refractive index of 1.5441 at 20°, and sp. gr. 1.035 at 15.5°, and boils at 237°.

## Estragol, $C_3H_5.C_6H_4.OH$

Estragol, or methyl-chavicol, is a constituent of tarragon, anise bark, bay, fennel and other essential oils. It is a strongly odorous oil having the following characters:

B. p. at 760 mm.................................... 216°
B. p. at 12 mm..................................... 98°
Sp. gr. at 15.5°.................................... 0.972
Ref. index at 20°................................... 1.5220

By means of cross naming (due to the fact that the allyl containing phenol when isomerised by alkali into the corresponding propenyl containing substance takes the name of the *iso*-phenol) anethol is also known as *iso*-estragol, as estragol is converted into anethol by means of alkali hydroxide. This reaction serves to identify estragol. If it be heated on a water bath for 24 hours with three times its volume of a saturated alcoholic potassium hydroxide solution, it is completely converted into anethol, which after recrystallisation from petroleum spirit in the cold, melts at 22°. Or if estragol be shaken in the cold with two-thirds of its weight of potassium permanganate dissolved in 100 times its weight of water, and its own weight of acetic acid, it yields homo-anisic acid which is neutralised with sodium carbonate, the liquid filtered and the acid set free with dilute sulphuric acid and extracted with ether. It melts at 85° to 86°.

**Anethol, 1–4-Propenylphenol Methyl-ether, $C_3H_5.C_6H_4OCH_3$**

Anethol occurs in admixture with more or less terpenes and other substances, in the essential oils of aniseed (*Pimpinella anisum*), staranise (*Illicium verum*), fennel, etc. It is deposited in crystalline plates when these oils are cooled. Anethol has an odour resembling that of oil of anise. It undergoes oxidation on keeping. Freshly prepared pure anethol congeals at about 21°, and remelts between 22.5° and 22.7°. It is optically inactive and boils at 232°. Its refractive index is 1.5615 at 18°. Anethol is only sparingly soluble in water, but dissolves easily in alcohol and ether. Anethol is readily polymerised by the action of sulphuric acid, stannic chloride, etc. By boiling with hydriodic acid, anethol yields methyl iodide and *anol*, $C_3H_5.C_6H_4.OH$, and by boiling with chromic acid mixture is converted into acetic acid and *anisic acid*, $C_6H_4(O.CH_3).COOH$. Anethol combines with bromine with production of a brom-anethol dibromide, $C_6H_3Br.(O.CH_3).(C_3H_5Br_2)$, which melts at 107°.

Anethol is best identified by oxidation to anisic acid by taking 5 grm. of the substance and heating it to 50° with a solution of 15 grm. of potassium dichromate, 50 grm. of sulphuric acid, and 100 c.c. of water. The mixture is well shaken, allowed to cool and the clear liquid is decanted. The solid deposit is well washed with

water and recrystallised from boiling water, when it melts at 184°.
Anethol dibromide $C_6H_4.O.CH_3.C_3H_5Br_2$ is another well defined
crystalline compound by which anethol can be identified.   It is
obtained by the action of bromine dissolved in chloroform, on
anethol.   It is recrystallised from petroleum spirit, and then melts
at 67°.

Anethol is of great importance commercially, as it is the raw
material from which anisic aldehyde, known as aubepine in com-
merce, is produced.   This substance (*q. v.*) forms the basis of all the
perfumes of the "New Mown Hay" type.

By boiling with alcoholic potassium hydroxide, methyl chavicol
undergoes a molecular rearrangement, with conversion into anethol.

### Safrol and Isosafrol, $C_{10}H_{10}O_2$

Safrol is the essential constituent of oil of sassafras, and is also
present in camphor oil, the oil from star-anise, etc.

Safrol is a colourless liquid, but when cooled sufficiently it crystal-
lises in large monoclinic prisms which melt at +11°.   Safrol is
neutral to litmus, optically inactive, and has a fragrant odour of
sassafras.

When gently heated with alcoholic potassium hydroxide safrol is
converted into *isosafrol*, the allyl group being isomerised to a pro-
penyl group.   *Iso*safrol is a liquid solidifying at very low tempera-
tures.   Both safrol and *iso*safrol yield an intense red coloration
when treated with strong sulphuric acid.   Safrol is not altered by
treatment with sodium, whereas *iso*safrol is readily reduced to
*dihydrosafrol*, $C_{10}H_{12}O_2$.

Safrol is now a commercial article on a very large scale.   It is
prepared entirely by the fractional distillation of crude brown
camphor oil, the residual product in the manufacture of cam-
phor.   This crude oil is rich in safrol, and the lower boiling
fractions consist of terpenes, etc.   The oil is sold on the basis
of its sp. gr. which, of course, varies according to the amount
of safrol present.

Commercial safrol is used as the basis of artificial oil of sassafras,
but its principal use is in the manufacture of the well known artificial
perfume, heliotropin.   It is used also to a very large extent as a
cheap soap perfume.

Safrol is isomerised by means of alcoholic potassium hydroxide into isosafrol, containing the propenyl group, and from the isosafrol resulting, heliotropin (*q. v.*) is prepared.

The two isomers have the following characters.

|  | SAFROL | ISOSAFROL |
|---|---|---|
| Sp. gr. at 15.5°............................... | 1.106 | 1.1255 |
| Ref. index at 20°............................... | 1.5385 | 1.5780 |
| M. p........................................... | $+11°$ | ............ |
| B. p. at 760 mm............................... | 233° | 254° |
| B. p. at 4 mm................................. | 91° | ............ |
| Opt. rot....................................... | $\pm 0°$ | $\pm 0°$ |

When safrol is oxidised it yields homopiperonylic acid, which melts at 128°. Five parts of safrol and 12.5 parts of potassium permanganate dissolved in 200 c.c. of water and 5 parts of acetic acid are heated to 70°–80° and the liquid then rendered alkaline. The filtered liquid is extracted with ether, and the residual liquid is boiled with magnesium carbonate, again extracted with ether, and the filtered residual liquid acidified with dilute sulphuric acid, and the separated homopiperonylic acid recrystallised from hot water. It melts at 127°–128°.

Safrol also yields a pentabromide $C_{10}H_5Br_5O_2$, m. p. 169°–170°. When isosafrol is oxidised with potassium permaganate, the principal oxidation product is heliotropin (piperonal), m. p. 37°.

With excess of bromine, isosafrol yields a pentabromide melting at 197°. If safrol, dissolved in carbon disulphide, be heated with bromine, it yields mono-brom-isosafrol-dibromide, $C_{10}H_9Br_3O_2$, melting at 109°–110°. The two substances have the following constitutions.



Safrol                    Isosafrol
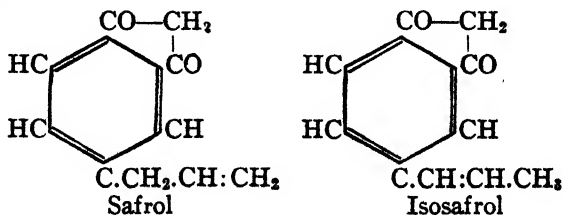
## Eugenol, $C_3H_5.C_6H_3(OCH_3).OH$

This substance is the chief constituent of oil of cloves, of which it forms from 75 to 95%. Eugenol also occurs in the oils of allspice, *Pimenta officinalis*, cinnamon leaves, and canella and massoya

barks. It is likewise present in the leaves of *Illicium religiosum*, and in small proportion in the oils of camphor, sassafras, and cinnamon bark.

For the preparation of eugenol, oil of cloves should be shaken with an alcoholic solution of potassium hydroxide, and the resulting mass pressed between folds of blotting-paper, washed with alcohol, and decomposed by dilute hydrochloric acid. Eugenol may also be prepared by agitating 3 volumes of oil of cloves with 10 volumes of a 5% solution of potassium hydroxide. The oily layer, consisting of hydrocarbons, etc., is separated, and the eugenol liberated from the aqueous liquid by acidifying it with hydrochloric acid or passing a stream of carbon dioxide through it. The eugenol is then washed by agitation with water and purified by distillation.

Eugenol may be obtained synthetically by the action of sodium-amalgam and water on coniferyl alcohol.

When freshly prepared, eugenol is a colourless, oily, highly refractive liquid of sp. gr. 1.070, having the characteristic smell and taste of cloves. It turns brown on exposure to air, and boils with slight decomposition at 252°. Its refractive index is 1.5439 at 20°.

Eugenol is very slightly soluble in water, but dissolves readily in alcohol, ether, and glacial acetic acid. It is also readily soluble in a dilute solution of alkali hydroxide. This character may be employed for the estimation of eugenol in oil of cloves, etc., and used as a test of its purity. When shaken with ammonia, eugenol is converted into a yellow crystalline mass of ammonium eugenate.

On adding 1 drop of strong sulphuric acid to 10 of eugenol a blue coloration is stated to be developed, changing, on addition of more acid, to a purple-red. Bromine vapour colours eugenol blue.

An alcoholic solution of eugenol gives a blue colour on addition of ferric chloride. It reduces ammoniacal silver nitrate, but not Fehling's solution.

Eugenol is stated to be a more powerful antiseptic than phenol. It can be taken internally in small doses without ill effects, but in larger quantities it occasions headache and vertigo. It passes into the urine as *eugenol-sulphonic acid*, which rapidly splits up into its constituents.

When boiled with alcoholic potassium hydroxide, eugenol is converted (incompletely) into *isoeugenol*, a compound in which the *allyl group* has undergone molecular rearrangement and conversion

into the *propenyl group*. *Iso*eugenol boils at 262° and is coloured olive-green by ferric chloride. Its sp. gr. is 1.088, and ref. index 1.5730 at 20°.

By the action of potassium permanganate, eugenol is oxidised, with formation of vanillin, homo-vanillin, and vanillic acid. Eugenol forms the starting-point of several commercial methods of preparing artificial vanillin, and is always first converted into *iso*eugenol.

Eugenol is now employed on a very large scale for the manufacture of vanillin, so that it has become an article of the highest commercial importance. It yields a characteristic benzoyl derivative when treated with benzoyl chloride in the presence of potassium hydroxide. Benzoyl eugenol melts at 69°–70°. It also forms a diphenyl-urethane m. p. 107°–108°.

Eugenol is invariably isomerised into isoeugenol in the process of vanillin manufacture; the isoeugenol is converted into acet-iso-eugenol by means of acetic anhydride, and this is oxidised to acetyl-vanillin, which is hydrolysed to vanillin.

Isoeugenol itself has a powerful carnation odour, considerably finer than the clove odour of eugenol, and is indispensable to the perfumer in the manufacture of all types of carnation odours. When cooled to a low temperature isoeugenol solidifies to a mass of fine needles, and melts at 34°. It, however, usually exists in a state of superfusion, and commercial isoeugenol is always liquid.

Isoeugenol forms a benzoyl compound when treated with benzoyl chloride and alkali hydroxide. Benzoyl-eugenol melts at 105°. It also yields a diphenyl-urethane, m. p. 112°–113°.

Methyl-eugenol, $C_{11}H_{14}O_2$, is a homologue of eugenol, existing in the essential oils of calamus, cassie, betel, bay leaves and others. It is also manufactured artificially, and is a valuable adjunct to the perfumer in the manufacture of carnation boquets, giving the resulting perfume a somewhat distinctive *"timbre."* It is prepared by the action of methyl iodide on eugenol-sodium. Its sp. gr. is 1.042 at 15.5°, ref. index 1.5380 at 20°, and b. p. 248°. Methyl-eugenol can be identified by conversion into veratric acid.

This compound is obtained by oxidising 6 grm. of methyl-eugenol by means of a solution of 18 grm. of potassium permanganate in 400 c.c. of water. When recrystallised from alcohol, veratric acid melts at 179°–180°. Methyl-eugenol also forms a bromine derivative, mono-brom-methyl-eugenol dibromide, m. p. 79°–80°.

This is prepared by dissolving 50 grm. of the phenol in 100 grm. of dry ether, and adding 30 c.c. of bromine drop by drop, keeping the mixture cold.

Methyl-isoeugenol occurs in the essential oil of *Asarum arifolium*, and is also obtained artificially in the same way as methyl-eugenol. It is a liquid, b. p. 263° and having a sp. gr. 1.062, and ref. index 1.5720. It yields veratric acid by oxidation, but by the action of bromine yields a dibromide, m. p. 100°–102°, which easily differentiates it from the isomeric methyl-eugenol.

The constitutions of eugenol and isoeugenol are as follows:



Eugenol                    Isoeugenol
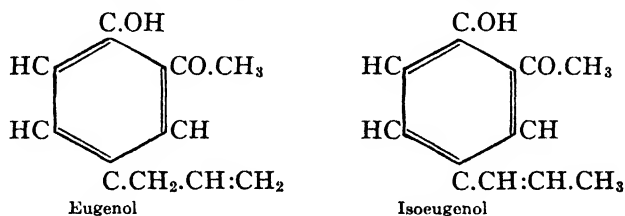
### Estimation of Eugenol

The estimation of eugenol is of practical importance for the valuation of oil of cloves and other essential oils, but is complicated by the presence of acet-eugenol, as well as free eugenol. Hence processes which estimate the free eugenol only, give lower results than those which effect, in addition, a partial or complete estimation of the combined eugenol.

J. C. Umney has proposed the following simple method for the estimation of the eugenol in oil of cloves (*Pharm. J.*, [3], 25, p. 950): A known quantity (10 c.c. at 15°, or 10 grm.) of the sample is mixed, in a 100 c.c. flask with a long narrow neck graduated in tenths of a c.c., with a 10% aqueous solution of potassium hydroxide, and the mixture vigorously shaken in the corked flask 5 or 10 minutes, when the eugenol will be dissolved. Water is then added till the floating stratum of non-phenolic constituents is brought into the neck of the flask, which should be warmed to assist in the separation of the unabsorbed caryophyllene. The liquid is finally cooled to 15°, the insoluble oil measured, and the volume multiplied by 0.908 (the approximate sp. gr. of caryophyllene). The weight of insoluble oil thus found is subtracted from the total weight of the oil used, the difference being the eugenol in the sample taken. The

results are usually somewhat high owing to the slight solubility of the sesquiterpene in the alkaline liquid and to the presence of combined eugenol in the oil, but by using 85 c.c. of a solution of potassium hydroxide of 5% strength, to 10 c.c. of the sample, E. C. Spurge finds that better results are obtainable. In practice, it is found that the oil globules adhere to the surface of the flask, and will only rise into the neck after prolonged standing—from 24 to 48 hours. The universal practice to-day is to use a 5% solution of potassium hydroxide.

In a method proposed by H. Thoms (*Ber.*, 1891, **24**, 283), which he has subsequently slightly modified, the eugenol is weighed as its benzoyl derivative. If the process be applied to the original oil, the amount found represents the free eugenol present, *plus* a variable proportion of eugenol ethers. Thoms has, however, recently modified the process which, when the free eugenol only is to be estimated, is carried out as follows: A weight of 5 grm. of the oil is dissolved in ether and rapidly shaken out, first with about 20 c.c., and then with another 5 c.c. of 15% aqueous sodium hydroxide solution. The mixed alkaline liquid is warmed to expel any dissolved ether, and the process then carried out as described below, the benzoyl chloride being added to the liquid.

When the oil is examined by Thoms' method *after saponification*, the result represents the total eugenol present. 5 gr. of the oil are heated on the water-bath for a short time (30 minutes) with 20 c.c. of a 15% aqueous solution of sodium hydroxide. Alcoholic alkali should not be employed, since the alcohol can only be completely removed with difficulty, and any remaining would affect the results by the formation of ethyl benzoate with benzoyl chloride. After saponification, the caryophyllene is separated from the alkaline liquid and washed twice with sodium hydroxide solution, the washings being added to the alkaline liquid. This latter is then treated with 6 grm. of benzoyl chloride. The mixture is well stirred or vigorously shaken for a few minutes, when much heat is developed. The action is completed on the water-bath, and the uncombined benzoyl chloride is volatilised by the heat. On cooling the liquid, crystalline benzoyl-eugenol separates. 55 c.c. of water is now added, and the liquid warmed until the compound melts and collects as an oil. The mixture is well stirred, then cooled, and the clear supernatant liquid filtered from the crystals. The washing is

repeated in this manner with 55 c.c. of water (making 160 c.c. in all). The crystalline mass is then transferred to a beaker with 25 c.c. of 90% alcohol, and warmed till complete solution takes place. The solution is then allowed to stand until the crystals have separated, and then cooled to 17°, and filtered through a paper 9 cm. in diameter, previously dried and tared. The filtrate measures about 20 c.c. and the crystals are washed with more alcohol until the filtrate measures 25 c.c. The paper and crystals are then dried in a weighing-glass and weighed, the temperature not rising above 101°. The solubility allowance for the alcohol is 0.55 grm. The total eugenol is calculated from the formula

$$P = \frac{4100(a + 0.55)}{67B}$$

where P is the percentage, $a$ the weight of benzoyl-eugenol, and B the weight of clove oil used.

The following method for the estimation of free eugenol in essential oils has been proposed by Verley and Bölsing (*Ber.*, 1901, **34**, 3354). The process depends on the fact that acetic and other anhydrides act vigorously upon phenols and alcohols in presence of excess of pyridine, and in many cases the combination of phenol and acid anhydride is quantitative and practically instantaneous. Eugenol reacts readily, forming eugenyl acetate and acetic acid, the latter being taken up by the pyridine, and pyridine acetate produced. This latter compound behaves to phenolphthaleïn exactly like acetic acid, and can therefore be titrated, since pyridine is unaffected by this indicator. From one to 2 grm. of the sample to be examined is introduced into a flask of 200 c.c. capacity, and 25 c.c. of a mixture of acetic anhydride and pyridine added. The mixture is made up by mixing 30 grm. of acetic anhydride with 220 grm. of *absolute* pyridine. No action takes place, but on the addition of water the anhydride is decomposed with formation of pyridine acetate, which is easily saponified by alkali. The whole is then heated for 15 to 30 minutes on the water-bath (a condenser is unnecessary), the liquid cooled, 25 c.c. of water added, and the mixture shaken. The acetic acid is then titrated with N/2 alkali hydroxide and phenolphthaleïn. A similar quantity (25 c.c) of the pyridine and acetic anhydride mixture is diluted with hot water and titrated direct. The difference in the volume of alkali required in the two titrations, multiplied by 0.582, gives the eugenol in the amount of sample taken.

According to E. C. Spurge (*Pharm. J.*, 1903, **2,** pp. 701, 757), none of the methods already described give strictly accurate results. He considers Verley and Bölsing's method to be rapid and simple, yielding an estimation of the free eugenol in clove oil within 1%.[1] The combined eugenol should be estimated by saponification. Spurge regards Thom's method as tedious but capable of improvement, though he prefers the method of Verley and Bölsing, or that of Umney when modified as already described, and corrected for the presence of esters in the oil, as estimated by saponification.

It must, of course, be recognised that the estimation of such substances as eugenol in oil of cloves can only, at best, be somewhat approximate, and the process which yields most concordant results, so that vanillin manufacturers can know exactly what an analytical certificate really means, is obviously the best process to employ. In a paper read before the International Congress of Applied Chemistry in 1912, J. C. Umney and E. J. Parry recommended the following as the details of the absorption process.

"Most satisfactory results are obtained by the use of a 5% solution of ordinary stick potassium hydroxide. Ten c.c. of the oil should be used in a flask of about 150 c.c. capacity. The specific gravity of the absorbed and unabsorbed portions is not usually taken into account, and we do not think it wise to introduce this correction, since it might vary considerably in different samples of the same type of oil."

Bennett and Garratt (*Perfumery and Essential Oil Record*, May, 1923, 139) have carried out a series of experiments on the estimation of phenols in various essential oils and conclude that the above recommendation is confirmed by their experiments. They found that pure eugenol yielded 98% to a solution of potassium hydroxide of 5% strength, and that the terpene and sesquiterpene mixture of oil of cloves yielded 3% to the same strength solution. Mixtures of eugenol and terpenes, etc., of clove oil in fixed proportions gave the following results, which show that the errors in solubility are fairly well balanced in actual practice.

| ACTUAL EUGENOL VALUE | 5 C.C. USED FOR ESTIMATION | 10 C.C. USED FOR ESTIMATION |
|---|---|---|
| 75% | 75% | 74% |
| 50% | 52% | 50% |
| 25% | 28% | 26% |

[1] Schimmel & Co. (*Report*, April, 1903), however, state that the method is unreliable, but their opinion is chiefly based upon the fact that Umney's method gave in their hands higher results on certain samples of clove oil than that of Verley and Bölsing. It has, however, been shown that Umney's method, when uncorrected, invariably gives high results in the case of clove oil.

McKie (*J. Chem. Soc.*, 1921, **119**, 777) finds that the melting point of the mixed benzoyl derivatives forms an accurate basis for estimating the percentage of eugenol and isoeugenol in a mixture of the two substances, an estimation frequently required by the vanillin manufacturer during the course of the isomerisation process. The crude mixture is converted into the benzoyl derivatives by means of benzoyl chloride in the usual manner, dried and purified. The melting points of various mixtures are given below:

| | MIXTURE, % | |
|---|---|---|
| ISOEUGENOL. | EUGENOL. | M. P. |
| 0 | 100 | 69.5° |
| 16 | 84 | 64° |
| 25.5 | 74.5 | 56.5° |
| 29 | 71 | 65.8° |
| 32 | 68 | 69.4° |
| 35 | 65 | 72.5° |
| 40 | 60 | 79.7° |
| 46.5 | 53.5 | 82.7° |
| 51.5 | 48.5 | 83.6° |
| 53.6 | 46.4 | 86° |
| 54.9 | 45.1 | 86.2° |
| 59.7 | 40.3 | 86.8° |
| 78 | 22 | 91.4° |
| 87.5 | 12.5 | 98.2° |
| 100 | 0 | 04° |

It is obvious that where there is about 25% of isoeugenol present the indication is valueless, but otherwise useful indications appear to be given.

### Asarol (Asarone), Propenyl-trimethoxy-benzene,

$$C_3H_5.C_6H_2(O.CH_3)_3$$

This compound forms the solid constituent of the oil of various species of *asarum*, and is also found in Matico oil. It crystallises in monoclinic prisms.

By the action of potassium permanganate, asarone is oxidised to *asarylic* (trimethoxy-benzoic) *acid*, m. p. 144°. With bromine, asarone melts at 62° and boils at 296°. Asarone yields a crystalline dibromide, m. p. 85° to 86°.

### Apiol, Allyl-dimethoxydihydroxybenzenemetnylene Ether

This compound, sometimes termed parsley camphor, occurs in oil of parsley (from *Petroselinum sativum*), in which it is present to the

extent of about 20%. An isomer of this substance, termed dillapiol, occurs in East Indian oil of dill, melting at 44° and boiling at 296°.

Apiol may be extracted from the seeds of the parsley plant by treating them with alcohol, and then extracting the residue with ether. Apiol crystallises from the ethereal solution on evaporation in long colourless needles, having a faint odour of parsley. It melts at 30° and boils at 294°.

Apiol is insoluble in water, but is very soluble in alcohol, ether, and in fixed and volatile oils. It does not combine with bases or acids, and does not react with hydroxylamine or phenyl-hydrazine.

When treated with oxidising agents, apiol is converted into *apiolaldehyde*, $C_{10}H_{10}O_5$, a small quantity of a volatile acid being simultaneously formed; and by prolonged treatment with potassium permanganate yields *apiolic acid*, $C_{10}H_{10}O_6$.

On boiling apiol with alcoholic potassium hydroxide, it is converted into *isoapiol*, in which the allyl group has been converted into the propenyl radicle. It melts at 56° and boils at 304°.

By the action of fuming nitric acid (sp. gr. 1.48) apiol is oxidised to oxalic acid and a crystalline golden-yellow nitro-compound, melting at 116°. By the action of bromine on a solution of apiol in carbon disulphide, *tribromapiol*, $C_{12}H_{11}Br_3O_4$, is formed and is obtained by crystallisation from alcohol in flat needles melting at 88°. Tribromapiol dissolves in concentrated sulphuric acid with violet colour.

*Commercial apiol* is an oily green liquid, containing a large proportion of true apiol. It varies considerably in density, colour, action of solvents, and heat. Pure apiol is volatilised unchanged by heat, but many commercial specimens are decomposed. The sp. gr. of apiol is usually from 1.050 to 1.080 at 15.5°.

The ordinary natural apiols are, therefore, ordinary parsley apiol which contains the allyl group, and dillapiol which also contains the allyl group, but differs from the ordinary apiol by the orientation of the side chains. Each is isomerised into its corresponding isomer with the propenyl group by heating for 12 hours with alcoholic potassium hydroxide.

Iso-dillapiol has also been found naturally to a small extent in the essential oil of *Piper acutifolium*.

The two apiols are represented by the following constitutions:

$$CO-CH_2$$
$$H_3C.O.C \diagdown CO$$
$$H.C. \diagup COCH_3$$
$$C.CH_2.CH:CH_2$$

Apiol

$$CO-CH_2$$
$$H_3C.O.C \diagdown CO$$
$$H_3C.OC \diagup CH$$
$$C.CH_2.CH:CH_2$$
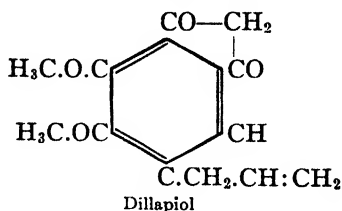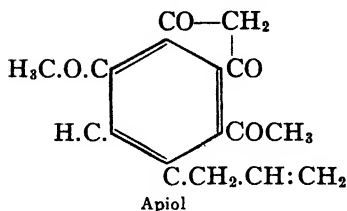
Dillapiol

The two substances have the following characters:

|  | APIOL | DILLAPIOL |
|---|---|---|
| M. p. | 30° | |
| B. p. | 294° | 285° |
| Sp. gr. at 15.5° | 1.1788 (superfused) | 1.1644 at 13°/4° |
| Ref. index at 200° | 1.5380 | 1.5278 at 25° |

Apiol is best identified by its melting point, and the melting point of isapiol, 56°, into which it is easily converted. To convert apiol into its aldehyde and acid for the purposes of identification, the following process should be employed. Four grams are dissolved in 40 c.c. of acetic acid and 5 grm. of chromic acid dissolved in 100 c.c. of acetic acid are added. After two hours, 1 litre of water is added, the mixture is neutralised with sodium hydroxide and then filtered. On being allowed to stand in a cold place, long needles of apiolic aldehyde are deposited, which, when recrystallised from alcohol, melt at 102°. To convert the phenol (either apiol or isoapiol) into apiolic acid, 8 grm. of the phenol are mixed in 800 c.c. of 5% sodium hydroxide, and then mixed with 30 grm. of potassium permanganate dissolved in 1600 c.c. of water. The mixture is heated on a water bath for an hour and then filtered. Unaltered phenol is extracted with ether. The mixture is then acidified with sulphuric acid and the precipitate is dissolved in hot water and filtered through animal charcoal. Apiolic acid melting at 175° separates.

When dillapiol is boiled with alcoholic potassium hydroxide for about 8 hours, the allyl group is isomerised to the propenyl group and isodillapiol results. This substance is a crystalline compound melting at 44° and boiling at 296°. On treatment with excess of bromine in acetic acid it forms monobrom-dillapiol-dibromide, m. p. 110°. On oxidation as above described, both dillapiol

and isodillapiol yield dillapiolic aldehyde melting at 75° and dill-apiolic acid melting at 152°.

## Chavibetol, $C_{10}H_{12}O_2$

Chavibetol, or allyl-guaicol, is a phenol occurring in the essential oil of betel, whose odour it possesses. It has the following characters:

B. p. at 760 mm................................. 254°–255°
B. p. at 12 mm................................. 131°–133°
Sp. gr. at 15.5°................................. 1.069
Ref. index at 20°................................. 1.5143
M. p................................. 8.5°

It yields a benzoyl derivative melting at 49°–50°.

## Diosphenol, $C_{10}H_{16}O_2$

Diosphenol is a colourless crystalline substance found in oil of buchu leaves melting at 83°–84°, b. p. 112° under 14 mm. pressure, and b. p. 232° at ordinary atmospheric pressure. It is optically inactive.

Diosphenol has at once the properties of a phenol and a ketone. It forms an oxime and a hydrazone. (See Semmler, *Ber.*, 1906, **39**, 1158.) Diosphenol may be extracted from oil of buchu by potassium hydroxide and is precipitated from the solution by acids. It gives a dark green coloration with ferric chloride.

Diosphenol forms a phenylurethane melting at 41°, a semicarbazone melting at 220° and a phenylurethane melting at 113°. The OH group possesses both alcoholic and phenolic functions. On reduction with sodium and alcohol, it yields an alcohol, $C_{10}H_{18}O_2$, melting at 159°.

Diosphenol has been prepared artificially by Semmler and McKenzie (*Ber.*, 1906, **39**, 1158) by the oxidation of oxymethylene-menthane. Its constitution is as follows:

$$C\text{---}CH_3$$
$$H_2C \quad \diagup\diagdown \quad COH$$
$$H_2C \quad \diagdown\diagup \quad CO$$
$$CH.CH(CH_3)_2$$
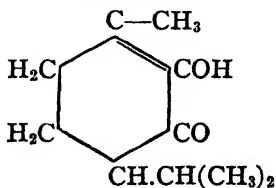
Asahina and Mituhori (*J. Pharm. Soc. Japan*, 1922, 255) have shown that menthone, when oxidised by ferric chloride yields diosphenol. They find that diosphenol yields an oxime melting at

123°, or by prolonged reaction a dioxime, m. p. 154°–157° (*J. Pharm. Soc. Japan*, 1923, 1).

A. C. Chapman (*Analyst*, 1900, 313) has described the following simple colour reactions for distinguishing between certain of these isomeric allyl- and propenyl-phenols. 1 c.c. of the highly purified phenol is dissolved in about 5 c.c. of acetic anhydride, and to the solution thus obtained (*a*) a small fragment of fused zinc chloride, or (*b*) 1 drop of strong sulphuric acid, is added:

| Eugenol | Isoeugenol |
|---|---|
| $H_2SO_4$....Brown at first, becoming quickly purple, and finally wine-red. | A rose-pink, quickly changing to a light brown. |
| $ZnCl_2$.....Pale yellow, the colour disappearing on standing. | Bright rose-pink coloration. |
| **Safrol** | **Iso-safrol** |
| $H_2SO_4$....A bright emerald-green colour, becoming brownish-green and finally brownish. | A faint transient pink, becoming reddish on standing. |
| $ZnCl_2$.....Pale blue, becoming less intense on standing, and finally light brown. | Pink, becoming brownish-pink and finally brown. |
| **Estragol** | **Anethol** |
| $H_2SO_4$....Purple, turning to indigo-blue, and then to bluish-purple. | No colour at first. After a short time a yellowish tinge. |
| $ZnCl_2$.....Blue-violet colour, which becomes deep mauve and finally brownish. | A pale yellow colour appearing slowly, which deepens on standing, and finally becomes brick-red. |

## The Estimation of Phenols

The almost universal method for the estimation of phenols is to shake a known volume of the oil containing the phenols with a solution of alkali hydroxide, which absorbs the phenols and leaves the non-phenolic residue floating on the surface of the liquid. If the absorption be carried out in a flask with a graduated neck (a so-called "cassia oil" flask) the unabsorbed residue can be read off and the quantitative result calculated.

This method, although it gives the best results obtainable, is only approximate, since the solution of alkali-phenol dissolves a small amount of the non-phenolic substances, and the non-phenolic residue retains a small amount of phenol. But for general purposes no better method is available, and the errors involved balance fairly evenly.

The process is carried out as follows:

Five to 10 c.c. (*cf. Eugenol*) are well shaken at intervals for half to one hour in a Hirschsohn flask, with a graduated neck, with a

5% caustic soda solution, the flask being kept immersed in a water bath at a temperature of 80°–100°, until absorption is complete. The unabsorbed residue is driven into the neck of the flask with excess of the alkali solution, and the unabsorbed residue is read off. The difference in the sp. gr. of the absorbed phenols and the unabsorbed oil should, strictly speaking, be taken into account. but as the error thus introduced is so small, it is not, in practice, taken account of.

There has been much discussion as to the strength of the alkaline solution which should be employed for this estimation. The most recent examination of this subject is that of Bennett and Garratt (*Perfumery and Essential Oil Record*, May, 1923, 138).

They point out that the non-phenolic constituents of all essential oils do not dissolve to the same extent in the alkali-phenol solution. This source of error is, however, unavoidable, if a standard strength be adopted. A series of experiments were carried out on thymol, the non-phenolic residue of thyme oil, and on mixtures of the two. The results showed that the nearest approximation to accuracy was obtained when 10 c.c. of the oil was used with 5% potassium hydroxide solution.

For the estimation of thymol Kremers recommends the following process:

Five c.c. of the oil are diluted with an equal volume of petroleum spirit and shaken with a 5% solution of potassium hydroxide solution until absorption is complete. The alkaline solution of thymol is made up to 100 c.c., with 5% caustic solution, and 10 c.c. of this is taken for the estimation. Decinormal solution of iodine is then added, and the thymol precipitated as a red-brown compound. In order to ensure that sufficient iodine has been added, a few drops are tested with dilute hydrochloric acid. If enough iodine has been added, the liquid is brown: otherwise it appears milky white owing to the separation of thymol.

The solution is then acidified with dilute HCl and made up to 500 c.c. From this 100 c.c. are filtered off and the excess of iodine determined by titration with sodium thiosulphate. For the purposes of calculation, every c.c. of N/10 iodine consumed is equivalent to 0.00375 grm. of thymol.

Redman, Weith and Brock (*J. Ind. Eng. Chem.*, 1913, **5,** 831) use the following modification of the above method.

About 50 c.c. of normal solution of sodium bicarbonate are placed in a glass stoppered bottle of 500 c.c. capacity and diluted with 100 c.c. of water. To this is added 15 c.c. of a solution containing as much of the phenol under examination as corresponds with about a $N/10$ solution. To this is added $N/30$ iodine in excess until a permanent brown colour remains. The excess of iodine should amount to about 20 c.c. The mixture is vigorously shaken for a minute, diluted with 50 c.c. of normal sulphuric acid and the excess of iodine titrated back with thiosulphate solution, 5 c.c. of a 20% solution of potassium iodide being added. In order to ensure the reaction proceeding rapidly, the mixture must be well shaken after adding the iodine solution. In order to ensure that any iodine which may have entered into the hydroxy group is again liberated, care must be taken that a little hydriodic acid is always present—which is ensured by the addition of the potassium iodide. Titration is not to be regarded as complete, until the blue colour with starch as indicator does not return for 10 minutes.

A method for the estimation of phenols has been described by Seidel (*J. Amer. Chem. Soc.*, 1912, **47,** 508), but possesses no advantages over those above described.

Schryver (*J. Soc. Chem. Ind.*, 1899, **18,** 6) proposes to estimate phenols by the use of sodamide, which is decomposed by phenols, with the separation of ammonia. As water also decomposes the amide, it is necessary to be sure that the sample examined is dry. His process is as follows:

About 1 grm. sodamide is reduced to a fine powder, washed by decanting it 2 or 3 times with a little benzene, and placed in a wide-mouthed flask of 200 c.c. capacity, connected with a separating funnel and an inverted condenser. From 50 to 60 c.c. of thiophene-free benzene is placed in this flask, and brought to boiling on a water-bath, a current of air freed from carbon dioxide being at the same time introduced, by means of a water-air pump, through the separating-funnel, which dips under the surface of the liquid. Ten minutes' boiling will remove the last traces of ammonia which may have adhered to the sodamide. About 20 c.c. of normal sulphuric acid are then placed in the ammonia absorption bottle. A solution of between 1 and 2 grm. of the phenol or essential oil under examination is then slowly added through the separating funnel to the boiling mixture of sodamide and benzene, the funnel

washed with a little benzene, and air aspirated through the boiling contents of the apparatus until all the ammonia in the receiver has been absorbed. This usually takes about 75 minutes. The excess of sulphuric acid in the receiver is then titrated with normal sodium carbonate, methyl orange being employed as indicator. The result is expressed either in percentages of phenol or, especially in the case of oils containing unknown phenols, by the "hydroxyl value," that is, the number of c.c. of normal sulphuric acid required to neutralise the ammonia generated from one gram of the material.

## (D) Sulphur Compounds in Essential Oils

A certain number of essential oils contain sulphur compounds, usually in the form of sulphides or thiocarbimides. The most important of these oils are those of black and white mustard-seeds, garlic, and spoonwort or scurvy-grass. The following table shows the botanical origin and principal constituents of the chief sulphuretted oils:

| Oil | Botanical origin | Principal constituents |
|---|---|---|
| Allium................ | Entire fresh plant of *Allium ursinum.* | Vinyl sulphide;[1] vinyl polysulphides; traces of a mercaptan and an aldehyde. |
| Asafœtida............ | Gum resin, *Ferula species....* | Compounds of the composition $C_7H_{14}S_2$; $C_{10}H_{20}S_2$; $C_6H_{16}S_2$; $C_{10}H_{18}S_2$; pinene; a sesquiterpene; and a substance of the formula $(C_{10}H_{16}O)n$ (page 339). |
| Garden cress.......... | Flowering herb, *Lepidium sativum.* | Benzyl isothiocyanate; benzyl cyanide. |
| Garlic (and many oils of the *Cruciferæ*). | Entire green plant, *Allium sativum.* | Allyl-propyl disulphide, $C_6H_{12}S_2$; di-allyl disulphide, $C_6H_{10}S_2$; compounds containing $C_6H_{10}S_3$ and $C_6H_{14}S_4$. Allyl sulphide and terpenes are not present.[2] |
| Hedge-garlic.......... | Root of *Alliaria officinalis...* | Chiefly allyl thiocarbimide. |
| Horse-radish.......... | Root of *Cochlearia armoracia.* | Allyl thiocarbimide. |
| Mignonette........... | Root (and leaves and stalks) of *Reseda odorata.* | Phenyl-ethyl thiocarbimide. |
| Mustard-seed (Black)... | *Brassica nigra, juncea,* etc... | Allyl thiocarbimide; cyanallyl; carbon disulphide. |
| Mustard-seed (White).. | *Brassica alba..............* | Acrinyl thiocarbimide; carbon disulphide. |
| Onion................ | Fresh herb and bulb, *Allium cepa.* | Allyl-propyl disulphide; allyl sulphide and terpenes are not present.[2] |
| Peppermint, American.. | Dried herb, *Mentha piperita.* | Dimethyl sulphide. |
| Spoonwort (s c u r v y-grass). | Flowering plant, *Cochlearia officinalis.* | Secondary butyl thiocarbimide. |
| *Thlaspi arvense........* | Herb or seed, *T h l a s p i arvense.* | Allyl thiocarbimide. |

[1] Vinyl sulphide, $(CH:CH_2)_2S$, is a liquid of characteristic odour. b. p. 101°, sp. gr. 0.9125. It may be obtained from fresh allium oil by fractional distillation, after a previous treatment with sodium, by which vinyl sulphide is unattacked at ordinary temperatures. Vinyl sulphide combines with 6 atoms of bromine to form the compound $(C.H_2Br_2)_2.S.Br_2$. Silver oxide converts vinyl sulphide into *vinyl oxide*, $(C_2H_3)_2O$.

[2] It is doubtful whether allyl sulphide occurs in nature. The oils of garlic, onions, *Thlaspi arvense,* etc., were stated when first examined to consist largely of allyl sulphide, but F. W. Semmler's researches (*Arch. Pharm., 230, 434*) have shown that this constituent is not present.

The only one of these sulphur compounds of much commercial importance is allyl-thiocarbimide, the chief constituent of oil of mustard. When pure this is a liquid of sp. gr. 1.023 at 15.5, ref. index 1.5285 at 20°, and boiling at 152°. A great deal of this substance is prepared artificially and used—either legitimately or dishonestly—in place of mustard oil.

The estimation of allyl-thiocarbimide is a matter of some importance. Various processes have been proposed, of which the following are the most trustworthy:

3 grm. of the oil and 3 grm. of alcohol are shaken in a flask with 6 grm. of a 10% solution of ammonia. The mixture should become clear after standing for a few hours, or rapidly by heating to 50°. Crystals of allyl-thiocarbimide are then deposited. After standing for a time the liquid is decanted and slowly evaporated in a tared capsule over a water-bath, more ammonia being added as the smell disappears. The crystals first separated are now added to those in the capsule, the flask being rinsed with a little alcohol, and the capsule and crystals dried to constant weight. The crystals should melt at 70°–74°, or they are too impure for reliance to be placed on the estimation. 116 parts of the allylthiourea correspond to 99 of thiocarbimide.

Gadamer (*Arch. Pharm.*, 1899 **110, 237**) proposes the following process: The mustard oil is dissolved in alcohol to form a 2% solution. 5 c.c. (4.2 grm.) of this are allowed to remain with 25 c.c. of N/10 solution of silver nitrate and 5 c.c. of ammonia for 24 hours, in a stoppered 50 c.c. flask. It is then made up to 50 c.c. with water and filtered from the precipitated silver sulphide. 25 c.c. of the filtrate are mixed with 4 c.c. of nitric acid and a few drops of ferric sulphate solution, and titrated with N/10 ammonium thiocyanate until the red colour of ferric thiocyanate appears.

From the excess of silver so estimated the amount of thiocarbimide can be calculated.

Schimmel & Co. prefer the following method (*Schimmel's Reports,* (*April*, 1904, 63; Oct., 1904, 59; *April*, 1906, 45): About 5 grm. of a 2% solution of the oil in alcohol are mixed with 50 c.c. of N/10 solution of silver nitrate in a 100 c.c. flask. 10 c.c. of 10% ammonia are then added and the mixture left for 24 hours, away from the light. The flask is then placed for 30 minutes in water at 80°, being repeatedly shaken, allowed to cool, and then filled to the 100

c.c. mark.    50 c.c. of the filtrate from the silver sulphide are titrated
with N/10 ammonium thiocyanate after adding 6 c.c. of nitric acid
and a small amount of iron alum.

The percentage of thiocarbimide is calculated from the formula

$$P = \frac{24.7875a}{b}$$

where P is the % of thiocarbimide, $a$ the number of c.c. of silver
nitrate solution which have been used in the reaction, and $b$ is the
weight of the 2% spirit of mustard used.

Brioux (*Ann. Chem. Anal. Appliquée*, **17**, 3) gives the following
method for the estimation of isothiocyanates in mustard flours and
oil cakes.    Twenty five grm. of the well ground cake or flour are
placed in a litre flask, 500 c.c. of distilled water added, and 2 grm.
of sodium fluoride dissolved in a little water.    The flask is closed,
and heated in a water bath for 3 to 4 hours to almost 40°.    Twenty
five c.c. of 95% alcohol are then added, and the liquid distilled from
a sand bath; 150 c.c. of the distillate are collected in a 250 c.c. flask
containing 10 c.c. of strong ammonia.    Then from 25 to 50 c.c. of
N/10 silver nitrate solution are added, and the flask heated for an
hour under a reflux condenser in a water bath maintained at about
85°.    When cold the liquid is made up to 250 c.c., shaken and filtered,
and 125 c.c. taken for the estimation of excess of silver by means
of N/10 ammonium thiocyanate.    Before making this titration,
10 c.c. of pure nitric acid and 10 c.c. of a 10% solution of iron alum
must be added.    From the quantity of silver necessary to precipi-
tate the sulphur as silver sulphide the amount of allyl thiocyanate
is easily calculated.    Huber and Van der Wielen (*Pharm. Weekblad*,
1915, 39) give the following method for estimating the thiocyanate
in mustard seeds.    Five grm. of the finely powdered sample are
macerated with 100 c.c. of water for two hours at ordinary tempera-
ture.    Twenty c.c. of alcohol is then added to arrest fermentation,
and 2 c.c. of olive oil.    About 50 c.c. is distilled into a 100 c.c.
measure containing 10 c.c. of ammonia, so that the delivery tube is
inserted in the ammonia solution.    After adding 20 c.c. of N/10 silver
nitrate solution, the mixture is heated on a water bath until the
silver sulphide has become aggregated and the liquid is quite clear.

The liquid is then cooled, made up to 100 c.c. with water, and the
excess of silver nitrate determined by titration with N/10 ammonium
thiocyanate, iron alum being used as indicator.    The time of macer-

ation is of considerable importance, as after about 2 hours the results become steadily lower, and after 24 hours, maceration, the results may be 30% to 40% too low.

## (E) ALDEHYDES

A large number of the aldehydes naturally existing in essential oils have become of the highest importance as commercial articles, and numerous artificially prepared aldehydes have, during the past few years, become indispensable to the modern users of essential oils, especially to the perfumer. A most interesting series of these substances is that of the fatty aldehydes, which have such an intense odour that they must only be employed in minute quantities. The more important of these are the following.

*Heptylic aldehyde.*—This substance, known also as oenanthylic aldehyde, is an oil of powerful fruity odour. It has a sp. gr. 0.820, at 15.5°, ref. index 1.4150, at 20°, and boils at about 155°. It forms an oxime, m.p. 50°.

*Octyl aldehyde* is a natural constituent of rose and neroli oils, and is also prepared artificially. It has a heavy honey-like odour, and is used in the preparation of mixed bouquet odours. It has a sp. gr. 0.821 at 15.5°, ref. index. 1.4195 at 20° and b. p. 82° at 13 mm. It yields an oxime, m. p. 60° and a semicarbazone, m. p. 101°.

*Nonyl aldehyde.*—This is an oil of odour recalling that of rose and to some extent orange, in both of which oils it occurs naturally. It has a sp. gr. 0.8277 at 1.55°, ref. index 1.4245 at 20° and b. p. 92° at 13 mm. Its oxime melts at 69° and its semicarbazone at 100°.

*Decyl aldehyde.*—This is also a constituent of rose and orange oils. It is probably the most useful of all the fatty aldehydes to the perfumer. It is an oil, b. p. 209°, and has a sp. gr. 0.828 at 15.5°, and ref. index 1.4297 at 20°. Its oxime melts at 69° and its semicarbazone at 102°.

*Duodecylic aldehyde* is generally similar to the last described, and is used for blending perfumes. It is a solid substance, m. p. 23–24° and b. p. 128° at 13 mm. Its semicarbazone melts at 102°.

There are a number of other aldehydes, some belonging to the saturated and some to the unsaturated series, which are used to some extent both for perfumery and flavoring essence manufacture. Hexylenic aldehyde, for example, is found in strawberry leaves, and is also prepared artificially. These higher fatty aldehydes are

used in minute amount in the manufacture of the more modern artificial flavouring essences especially those of strawberry, raspberry, peach, apricot, etc. The aldehydes of the geraniol series, which are of very considerable commercial importance, may now be discussed. These are entirely natural products and are not artificially made commercially.

## Citral and Neral

Citral, also known as geranaldehyde, is usually spoken of as a definite compound, and for most practical purposes it may be so regarded. It is now clear, however, that 2 stereoisomeric forms of citral exist, both being present in lemon-grass oil, which forms the principal source of commercial citral. (See under Nerol.)

Citral forms 70–85% of lemon-grass oil, and is present to the extent of about 4 to 6% in lemon oil. The oil of *Backhousia citriodora* also contains a large amount of citral, up to 95%.

Commercially, citral is of great importance, as it is the starting-point for the manufacture of ionone and allied compounds, which are the basis of the artificial violet perfumes so commonly used at the present time. Citral is a colourless or pale yellow liquid having a sp. gr. 0.890 or thereabouts. Commercial samples usually have a sp. gr. rather higher than this, due to the presence of a small quantity of impurities. It boils at 228°–230° at ordinary pressure, and at 110° at 12 mm. Its refractive index is about 1.4900, and it is optically inactive. The properties of the two isomers in a state of purity have been determined by Tiemann. The isomerism appears to be due to the relative space positions of the −CHO group and the H atom attached to a carbon atom in the molecule. This can be seen by an examination of the corresponding formulæ for geraniol and nerol, of which α-citral and β-citral are the aldehydes, respectively.

Tiemann's figures are as follows:

|  | α-citral | β-citral (neral) |
|---|---|---|
| Sp. gr.............................. | 0.8898 | 0.8880 |
| B. p. at 20 mm....................... | 118° | 118° |
| Ref. index at 20°..................... | 1.4891 | 1.4900 |

$\alpha$-Citral yields a semicarbazone melting at 164°, while that of its isomer melts at 171°.

Citral forms a condensation product with cyanacetic acid, citral-idene-cyanacetic acid, $C_9H_{15}.CH:C(CN)(COOH)$, m. p. 122°.

The methods of estimating citral are described on page 519 *et seq.*

Citral behaves similarly to citronellal (*vide infra*) when treated with molecular proportions of pyroracemic acid and $\beta$-naphthyla-mine. The citral-$\beta$-naphthocinchoninic acid obtained forms lemon-yellow laminæ, m. p. 199°–200°.

F. Tiemann has pointed out (*Ber.*, 1898, **31**, 3324) that if the citral is not present in theoretical proportion, the pyruvic or pyroracemic acid is partially decomposed, and $\alpha$-methyl-$\beta$-cinchoninic acid is formed, melting at 210°. In addition, a neutral substance is produced, which can only be separated by repeatedly dissolving the acid in ammonia, and reprecipitating it by acetic acid. Pure citral gives about 45% of the theoretical yield (or nearly its own weight) of citryl-$\beta$-naphtho-cinchoninic acid. If Doebner's reaction be applied to a mixture of citral and citronellal, the citryl compound crystallises out first, and citronellyl-$\beta$-naphtho-cinchoninic acid, melting at 225°, can be obtained from the mother-liquor. Tiemann states that 10% of citronellal in citral can be detected with certainty in this manner.

By treatment with hydriodic acid or potassium hydrogen sulphate citral is converted quantitatively into *cymene*, $C_{10}H_{14}$. This reaction confirms the constitutional formula already given.

When treated with silver oxide and ammonia, citral is converted into the corresponding acid, *geranic acid*, $C_{10}H_{16}O_2$.

The probable formulæ for the two isomers are either

$$\begin{array}{c} CH_3 \\ {\phantom{CH_3}} \\ CH_3 \end{array}\!\!\!\!>\!C:CH.CH_2.CH_2.C(CH_3):CH.CHO$$

or

$$\begin{array}{c} CH_2 \\ {\phantom{CH_2}} \\ CH_3 \end{array}\!\!\!\!>\!C.CH_2.CH_2.CH_2.C(CH_3):CH.CHO.$$
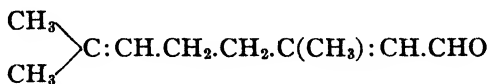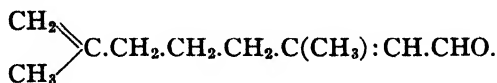
### Citronellal and Rhodinal

Citronellal occurs in large proportion (30 to 50%) in oil of citron-ella, and in certain kinds of geranium oil. It is also present in the oil of *Eucalyptus maculata* (var. *citriodora*).

Rhodinal appears to be a definite substance isomeric with citronellal, and the formulæ for the two are probably as follows:

$$\begin{matrix} CH_3 \\ \phantom{xx} \\ CH_2 \end{matrix}\Big\rangle C.CH_2.CH_2.CH_2.CH(CH_3).CH_2.CHO$$

Citronellal

$$\begin{matrix} CH_3 \\ \phantom{xx} \\ CH_3 \end{matrix}\Big\rangle C:CH.CH_2.CH_2.CH(CH_3)CH_2.CHO$$

Rhodinal
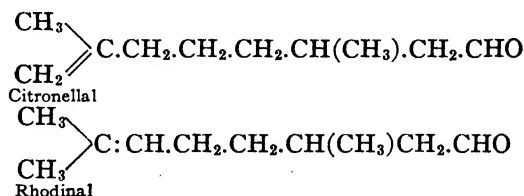
Citronellal is a colourless oily liquid, of agreeable citronella-like odour. It is optically active ($[a]_D$ = about ± 12°),[1] has a sp. gr. of 0.854 at 17.5°, and a ref. index of 1.4481 at 20°. It boils and distils with slight decomposition between 205° and 208°. It is almost certainly a mixture of the two isomers.

The purest commercial specimens have characters falling within the following limits:

B. p. .................................... 205°–208°
Sp. gr. at 15.5°. ........................... 0.855–0.858
Opt. rot. .................................. +10° to +12°
Ref. index at 20°. .......................... 1.4450 to 1.4485

By the action of reducing agents (sodium amalgam), citronellal is converted into the corresponding alcohol, *citronellol*, $C_{10}H_{19}.OH$.

When heated with acetic anhydride, citronellal is converted into the isomeric cyclic alcohol, *isopulegol*, closely resembling pulegol.

Labbé states (*Ber.*, 1899, **32,** 3338) that pure citronellal is apt to undergo complete and rapid isomeric change into *isopulegol*.

Citronellal was formerly regarded as a ketone, and hence was designated *citronellone*, but its aldehydic constitution was established by a reaction observed by O. Doebner (*Ber.*, 1894, **27,** 352), which depends on the formation of *citronellyl-β-naphthocinchoninic acid*. This compound is prepared by treating citronellal (more than 1 molecule), dissolved in absolute alcohol, with a solution of 1 molecule of pyroracemic (pyruvic) acid in the same menstruum, and adding a solution of 1 molecule of β-naphthylamine in absolute alcohol. The mixture is heated on a water-bath for 3 hours and then allowed to cool, when the acid crystallises out in colourless needles melting at 225°. Doebner recommends the reaction for the detection and estimation of citronellal in essential oils.

[1] According to Tiemann and Schmidt (*Ber.*, 1896, **29,** 903), citronellal exists in 2 optically opposed modifications, which on oxidation with chromic acid mixture yield the corresponding dextro- and lævo-*β-methyladipic acids*, (CO.OH)CH₂.CH₂.CH(CH₃).CH₂.CO.OH. Acetone is simultaneously formed.

Citronellal reacts violently with free sulphurous acid, terpenes and other products being formed, and a similar action takes place with sodium hydrogen sulphite containing free acid. The compound, $C_9H_{17}.COH,NaHSO_3$, is best prepared by treating the aldehyde with an ice-cold solution of neutral sodium sulphite to which the calculated quantity of acetic acid has been added. So prepared, and purified by kneading with alcohol and washing with ether, the compound is quite stable. It is quantitatively decomposed by sodium hydroxide or carbonate at the ordinary temperature. By the action of bisulphite solution, containing sulphite, on citronellal or its bisulphite compound, a compound is formed having the formula $C_9H_{18}(SO_3Na).CH(OH).SO_3Na$. By the action of sodium carbonate this is converted into the *hydrosulphonate*, $C_9H_{18}(SO_3Na).$-CHO, from which sodium hydroxide does not liberate citronellal, even on boiling.

On treatment with hydroxylamine, citronellal yields an *oxime*, $C_{10}H_{18}NOH$, as an oil of 0.906 sp. gr., b. p. 135° at 14 mm. pressure.

H. E. Burgess has observed (*Analyst*, 1900, 265) that citronellal gives a bright yellow colour, which is fairly permanent, when a little of the aldehyde is shaken with 2 or 3 times the quantity of a 10% solution of mercuric sulphate in diluted sulphuric acid (25%). Citral gives a bright red evanescent coloration.

## Estimation of Citral and Citronellal

The estimation of citral in essential oils is attended with peculiar difficulties.[1] Theoretically it should be possible to reduce the aldehyde to geraniol, which could then be acetylated and saponified, and a process on these lines has been described by H. Garnett (*Pharm. J.*, **56**, 321), but the alteration cannot be relied on to take place quantitatively. Every change is accompanied by the formation of by-products of resinification, such as methyl-heptenone, acetone, cymene, etc. This is the case even when the reduction of the citral to geraniol is conducted in alcoholic solution. The usual process based on the formation of the acid sulphite compound of citral is also open to criticism, owing to the unavoidable formation of soluble sulphonic compounds. Hence the method may be useful for ascertaining the comparative value of commercial samples of

[1] Except in cases such as that of lemon-grass oil, which contains a large proportion of this aldehyde.

oils containing citral, but not for the accurate estimation of the proportion of aldehydes unless they are present in large amount.

The condensation product of citral with cyanacetic acid has been described by F. Tiemann (*Ber.*, 1898, **31,** 3329) as a readily crystallisable compound, well adapted for the detection and estimation of citral in essential oils. A solution of cyanacetic acid in 3 parts of water is mixed with 2 equivalent proportions of sodium hydroxide (in the form of a 30% solution), and 1 equivalent proportion of citral then shaken with the alkaline liquid. Pure citral dissolves completely, and on acidifying the liquid, the citralidene-cyanacetic acid separates as an oil which soon becomes crystalline. The product, which is from 90 to 95% of the theoretical, is recrystallised from warm benzene or from a mixture of benzene and petroleum spirit, when a yield of 73 to 75% of the theoretical is obtained, the resulting yellow crystals melting at 122°, and having the composition $C_9H_{15}.CH:C(CN)COOH$. The citral in essential oils may be estimated by shaking the oil with an alkaline solution of the cyanacetic acid. After repeatedly shaking out the alkaline liquid with ether, the citral compound is liberated by acidifying the liquid.

E. J. Parry first concentrates the oil to be examined for citral (lemon oil) by distilling off about 85% of the terpene at a pressure of 12 to 13 mm. The distillate contains only the merest traces of citral. 200 c.c. of the oil thus yields about 25 c.c. of concentrated residue, the sp. gr. of which is first determined. 10 c.c. of the liquid is then shaken with a solution of about 5 grm. of cyanacetic acid and an equal weight of sodium hydroxide in 30 c.c. of water, the operation being performed in a small absorption flask having a long, graduated neck. The unabsorbed portion of the oil is measured,[1] and the percentage of citral thus obtained, after correcting for the sp. gr. of citral (0.897). The sp. gr. of citral is so near to that of the concentrated oil that they may be taken as identical. Parry states that the method has given fairly accurate results in his hands and the value of the method has been confirmed by Schimmel & Co. The cyanacetic acid must, however, be *quite* fresh, as there is reason to believe that it changes on keeping and then gives erratic results.

F. Tiemann (*Ber.*, 1898, **31,** 3297) has shown that the reaction of citral with alkali-metal sulphites varies with the conditions of the

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[1] A little trouble in measurement sometimes occurs, owing to the stearoptene of the oil forming a layer on the surface of the liquid, but in the author's opinion the difficulty is trifling. It may be wholly overcome by steam-distilling the citral from the concentrated residue, and operating on the steam distillate.

experiment. Thus on agitating 100 parts of citral with 100 of sodium hydrogen sulphite dissolved in 200 parts of water and 25 parts of glacial acetic acid, the normal bisulphite compound, $C_9H_{15}.$-$CHO,NaHSO_3$, is formed quantitatively. Partial dissociation occurs on dissolving the compound in warm water, and on regenerating the citral a loss of from 10 to 15% always occurs from a partial conversion of the normal compound into a hydrosulphonic acid derivative. A stable dihydrosulphonate, $C_9H_{17}(SO_3Na)_2.CHO$, not decomposed by alkali-metal carbonates or hydroxides, is obtained by the action of excess of bisulphite solution (which must be maintained acid throughout) on the hydrogen sulphite compound. An unstable dihydrosulphonate of the same formula as the above is obtained by the action of a slightly alkaline solution of sodium sulphite on citral or its normal bisulphite compound. For its formation, Tiemann recommends that 100 parts of citral should be shaken with 350 parts of sodium sulphite, $Na_2SO_3$, $7H_2O$, and 125 parts of sodium bicarbonate for several hours. The product is then extracted with ether to remove non-aldehydic impurities, and the citral liberated by sodium hydroxide. The solution of alkali should be previously saturated with ether, a layer of ether poured on the aqueous solution, and the sodium hydroxide added gradually, so as to expose the citral to its action for as short a time as possible. Tiemann recommends this process for the estimation of citral in lemon-grass oil. Under the prescribed conditions, geraniol and linalol do not form hydrosulphonates, while citronellal is converted into sodium citronellylhydrosulphonate, which is not decomposed by sodium hydroxide, even on boiling.

Tiemann gives the following results of estimation of citral in sample of lemon-grass oil by 3 methods:

|  | Cyanacetic acid method, % | NaHSO₃ method, % | Na₂SO₃ and NaHCO₃ method, % |
|---|---|---|---|
| Non-aldehydic constituents. | 18, free from citral | 24 citral present | 20, containing a little citral |
| Citral, by difference........ | 82 | 76 | 80 |
| Citral, by direct determination.................. | 75.4 | 65 | 77.5 |
| Citral, loss in direct determination.............. | 6.6 | 11 | 2.5 |

The cyanacetic acid method is to be preferred where the estimation of the non-aldehydic constituents is desired and the alkaline sulphite method for the estimation of the actual citral.

F. Tiemann states that the last method has the advantage that citronellal does not affect the estimation of the citral, but he denies the statement of Flatau and Labbé that a notable proportion (6 to 8%) of citronellal is present in lemon-grass oil.[1]   Tiemann (*Ber.*, 1899, **32,** 812) also points out certain differences in the behaviour of citral and citronellal with sulphites which may be utilised for their separation.   Thus citronellal is not attacked by a 10% solution of sodium sulphite ($Na_2SO_3.7H_2O$) in presence of sodium bicarbonate, and hence may be extracted together with the nonaldehydic substances by ether, whereas citral is completely converted under the same conditions into the unstable dihydrosulphonate already described.   On the other hand, if a mixture of the aldehydes is shaken with excess of *concentrated* sodium sulphite and bicarbonate solutions, citronellal is converted into the normal bisulphite compound, which separates, and citral into the unstable dihydrosulphonate.   If in this process the theoretical quantity or only a slight excess of sulphite is used, the citral compound is formed by preference, and the citronellal can be extracted unchanged by ether.   By applying the process to lemon-grass oil, and shaking the residue freed from citral with a concentrated solution of sodium sulphite and bicarbonate, Tiemann obtained 0.2 grm. of the citronellal bisulphite compound from 300 grm. of oil.   If a mixture of the aldehydes is shaken with sodium sulphite solution while a current of carbon dioxide is passed through it, the citral is converted into the unstable dihydrosulphonate, while the citronellal forms the hydrosulphonate, which is not decomposed by sodium hydroxide.   If methyl-heptenone is also present (as in lemon-grass oil), the citral may be extracted by a 10% solution of sodium sulphite containing bicarbonate, the citronellal by a concentrated solution of the same kind, and finally the methyl-heptenone by an ice-cold solution of sodium bisulphite in 1.5 parts of water.

Doebner recommends the following process for the separation of citral and citronellal.   The mixture of aldehydes is digested with pyruvic acid and β-naphthylamine, when condensation products of the aldehydes and β-naphthocinchoninic acid are formed.   The

[1] According to Flatau and Labbé (*Bull. Soc. Chim.*, 1898, **19,** 1012; 1899, **21,** 77), if the normal bisulphite compounds of citral and citronellal are treated with a solution of barium chloride, cityrl sulphite remains in solution whilst the citronellal is precipitated quantitatively as $Ba(SO_3.C_{10}H_{19}O)_2$, but Tiemann (*Ber.*, 1899, **22,** 812) states that the normal bisulphite compound of citral gives a copious precipitate with barium chloride, though the precipitation is not complete; whilst the precipitation of the normal citronellal compound is not perfect.

citral compound is less soluble than the citronellal compound and can easily be crystallised out first. The citral compound melts at 197°, while the citronellal compound melts at 215°.

Burgess and Child (see also under Aldehydes, p. 525) have adopted the following modifications of the bisulphite method and of the sulphite method of F. Tiemann for the estimation of the aldehydes (citral, etc.) in lemon oil. Both methods are stated to yield almost theoretical results when the following details are adhered to carefully:

1. In the estimation of the aldehydes by the sodium hydrogen sulphite method, a 40% solution of the reagent is most convenient, and a strongly acid solution should be avoided. 25 c.c. of lemon oil is mixed with 75 c.c. of 40% sodium metabisulphite solution and 25 c.c. of sodium sulphite (made by exactly neutralising sodium hydrogen sulphite solution with a 10% solution of sodium hydroxide) in a suitable flask. (See *Analyst*, 1900, 197.) The temperature is then raised to about 70° and the solution thoroughly shaken for 1 hour. The addition of sodium sulphite is indispensable, owing to the fact that it forms a soluble sulphonic compound and a clear meniscus is thus obtained. The oil is then raised into the measuring burette, and the diminution in volume gives the amount of total aldehydes.[1] A correction must be made for the solubility of the terpenes in solution. Burgess and Child subtract 0.35 c.c. from the reading, but it is advisable for each worker to determine this correction.

2. The following method depends upon the fact, discovered by F. Tiemann, that if citral is agitated with a neutral solution of sodium sulphite, a soluble sodium sulphonic acid salt is produced. Burgess and Child have taken advantage of the formation of sodium hydroxide in the reaction to make an addition

$$C_9H_{15}.CHO + 2Na_2SO_3 + 2H_2O = C_9H_{17}.(NaSO_3)_2.COH + 2NaOH$$

of phenolphthalein to the solution, to indicate the point when all the citral has combined to form the soluble compound. For the estimation a saturated solution of sodium sulphite is prepared, and, if acid, is neutralised with a solution of sodium hydroxide until a faint pink colour is permanently maintained with phenolphthalein. To 50 c.c. of this solution 25 c.c. of the oil is added, and 2 drops of an alcoholic solution of phenolphthalein. The whole is then heated on the water-bath nearly to b. p., with constant shaking. A deep

[1] This method may also be used for solutions containing high percentages of citral, using from 5 to 20 c.c. of the solution and measuring in a Hirschsohn or similar flask.

red colour almost at once appears, showing that the action has commenced. A few drops of sulphurous acid are then cautiously added, and the heating continued until no further colour is produced after a further addition of the sulphurous acid. Acetic acid, however, is preferable to sulphurous acid. The oil is then measured as described above. The obvious advantage of this method is that the end of the reaction may be ascertained to a certainty, whilst the bisulphite process depends on the continual shaking for a period of not less than 1 hour.

Sadtler (*J. Soc. Chem. Ind.*, 1905, **24,** 1193) proposes the following method.

Introduce into a counterpoised 150 c.c. flask, by means of a pipette, about 15 c.c. of oil of lemon, and note the exact weight; add 5 c.c. of distilled water and a few drops of rosolic acid test solution, and then neutralise the liquid exactly by the cautious addition of N/10 sodium hydroxide. Add 25 c.c. of a neutral solution of sodium sulphite (1 in 5) and immerse the flask in a water-bath containing boiling water. From a burette add, as needed, just sufficient N/2 hydrochloric acid to maintain the neutrality of the mixture, keeping the flask continuously heated and frequently agitated, and adding a drop or two of rosolic acid. When a permanent condition of neutrality is reached, note the number of c.c. of the N/2 hydrochloric acid consumed. Carry out a blank test, identical with the foregoing, except that the oil of lemon is omitted, and note the amount of N/2 hydrochloric acid consumed. Subtract the number of c.c. required in the blank test from the number required in the original test; each c.c. of this difference corresponds to 0.03802 grm. of citral. To find the percentage, multiply the above difference by 0.03802, and this product by 100, and divide by the weight of the oil of lemon taken.

Other processes for the estimation of citral in essential oils have been suggested, of which the formation of the oxime with hydroxylamine in alcoholic solution and subsequent titration of the excess of hydroxylamine with hydrochloric acid is the most useful and is now generally employed.

⟋The chief fault of the hydroxylamine process is that the end-point is not as well defined as could be desired. The most useful process is that described by Walther (*Pharm. Cent.*, 1899, **40,** 621), slightly modified by Bennett (*Analyst*, **34,** 394, 14)

The process is carried out as follows:

20 c.c. of a solution of hydroxylamine hydrochloride in 80% alcohol (half-normal strength), are exactly neutralised to phenolphthalein with a solution of sodium hydroxide in alcohol, and added to 20 c.c. of lemon oil (for example) and 20 c.c. of alcohol. The mixture is boiled gently under a reflux condenser for half an hour and allowed to cool. The condenser is washed down, and the contents of the flask diluted to 200 c.c. with water, and neutralised to phenolphthalein. The liquid is then titrated with N/2 sulphuric acid using methyl-orange as indicator. A blank experiment is carried out at the same time, and the necessary deduction made. Each c.c. of acid used for the neutralisation represents an equivalent amount of hydroxylamine that has combined with the citral, and is equivalent to 0.076 gr. of citral. The end-point is best determined by spotting on a white plate. It is distinctly sharper in this way.

Walther originally proposed to use sodium hydrogen carbonate to neutralise the hydrochloric acid of the hydroxylamine salt, but it is probable that the liberated $CO_2$ carries off a little hydroxylamine.

Burgess and Child obtained the following results by the foregoing methods (*J. Soc. Chem. Ind.*, 1901, **20**, 1179):

| Nominal % of citral in lemon terpenes | Sodium bi- and mono-sulphite I | Sodium sulphite II | Hydroxyl-amine III | Cyanacetic[2] acid IV |
|---|---|---|---|---|
| 2.5........................ | 2.2 (2.1)[1] | 2.2 (2.1)[1] | 2.6 (2.4)[1] | .......... |
| 5.0........................ | 4.4 (4.2) | 4.0 (4.2) | 5.0 (4.8) | .......... |
| 7.5........................ | 6.5 (6.3) | 6.4 (6.3) | 7.1 (7.2) | .......... |
| 10.0........................ | 8.6 (8.6) | 8.4 (8.6) | 9.6 (9.6) | .......... |
| Commercial citral............ | 84 % | 84 % | .......... | 100% |
| Terpeneless lemon oil......... | 46.5% | 45.5% | 46.6% | 62%[3] |
| Lemon-grass oil.............. | 75 % | 75 % | .......... | 97 % |

[1] The figures in parentheses show the calculated citral present.
[2] See E. J. Parry (*J. Soc. Chem. Ind.*, 1901, **20**, 1182).

Kleber (*American Perfumer*, 1912, 284) recommends the following process in which phenylhydrazine is the reagent employed. About 10 grm. of lemon oil are used, with 20 c.c. of a 5% freshly prepared alcoholic solution of phenylhydrazine. The flask is closed and allowed to stand for 30 minutes, and the mixture neutralised with N/2 hydrochloric acid. The neutral mixture is transferred to a

separator, the flask rinsed out with 20 c.c. of water and the whole well shaken.   On standing two layers separate, the lower one being drawn off, and the upper one washed with 5 c.c. of water, which is added to the liquid already drawn off.   The liquid is titrated with N/2 soda solution, with the use of ethyl-orange as indicator.   Each c.c. of N/2 alkali corresponds to 0.076 grm. of citral.

### Estimation of Citral

Various colorimetric processes of estimating citral have recently been devised.   Of these, the following give fairly accurate and concordant results.

**Hiltner's Method.**—R. S. Hiltner (*J. Ind. Eng. Chem.*, 1909, **1**, 798) bases a method on the fact that solutions of *m*-phenylenediamine hydrochloride give a yellow colour with solutions of citral, the intensity being dependent on the amount of citral present. This solution, which preferably should be freshly prepared each time, must be quite clear and colourless, and, if necessary, should be made so by treating it with animal charcoal and filtering.   The percentage of citral in the extract or oil under examination is estimated by comparative tests with a solution of known citral-content (0.25 grm. citral to 250 c.,c. dissolved in 50% alcohol).

The test is carried out as follows: 1.5 to 2 grm. lemon oil, or 25 grm. of lemon-extract are diluted to 50 c.c. with 90 to 95% alcohol; 2 c.c. of this solution are poured into the colorimeter-vessel, 10 c.c. *m*-phenylenediamine solution added, and the whole made up to a fixed volume.   Comparative tests are made simultaneously in the same manner with the standard solution referred to above, until the precise shade of colour of the solution under examination is reached.   The citral-content of the oil or extract of lemon can be calculated from the quantity of the standard solution taken up in the test.   If the citral-content is less than 0.1%, it will be desirable to use a little more of the solution under examination, in order to obtain the intensity of colour which is necessary to give exact results.

**Chace's Method.**—Chace (*J. Amer. Chem. Soc.*, 1906, **28**, 1472) has devised a method depending on the property of fuchsine-sulphurous acid of giving a red coloration in the presence of aldehydes. The solution of fuchsine-sulphurous acid is prepared as follows:

0.5 grm. of fuchsine is dissolved in 100 c.c. of water and a solution containing 16 grm. of $SO_2$ is added and when decolourised the whole

is made up to 1000 c.c. The solution must be freshly prepared, that is, not more than 3 or 4 days old. Alcohol of 95% strength is freed from aldehyde by keeping it in contact with caustic alkali for several days and then distilling, and boiling the distillate with 25 grm. of *m*-phenylenediamine per litre, for a few hours under a reflux condenser. The alcohol is then finally redistilled. A standard solution of 0.1% of citral in 50% alcohol is prepared. A quantity of the oil or essence containing about 0.1 to 0.2 grm. of citral is diluted to 100 c.c. with 50% aldehyde-free alcohol. 4 c.c. of this solution are used for the estimation, and are mixed with 20 c.c. of alcohol and 20 c.c. of fuchsine-sulphurous acid solution, and made up to 50 c.c. with alcohol. After well mixing, the observation tube is kept at about 15° and the colour compared with the necessary standards, from which the amount of citral can be calculated.

**Little's Method.**—Little (*Amer. Perfumer*, 1914, 74) prefers the following method depending on the use of diaminophenol.

The method is easily manipulated and can be conducted at room temperature:

*Reagent.*—Dissolve 0.2 grm. diaminophenol hydrochloride (commercially known as amidol), in 100 c.c. of 65% by volume alcohol, preferably distilled over potassium hydroxide. The use of aldehyde-free alcohol does not seem to make any difference in the results, as acetaldehyde has no apparent effect upon the reagent. The reagent is very readily soluble in 65% alcohol.

*Standard Citral Solution.*—A solution of pure citral in 50% alcohol, containing 0.001 grm. per c.c.

*Solution of Essence or Extract of Lemon.*—Weigh from 15 to 25 grm. of the extract for examination, and dilute to 30 or 50 c.c. with 50% alcohol, if a terpeneless extract, making a 50% solution.

Place 2 c.c. of the standard citral solution measured from an accurately graduated pipette, in a 250 mm. colorimeter tube, add 20 c.c. of 65% alcohol, and 15 c.c. of diaminophenol reagent and make up to 50 c.c. with 65% alcohol. Place 2 c.c. of the extract in the other tube with 15 c.c. of the reagent and make up to 50 c.c. with 65% alcohol as before, mixing the contents of both tubes thoroughly and allowing both tubes to remain for 5 to 10 minutes at room temperature, when the maximum colour is reached in both the citral tube and the extract under examination. The reading and calculation are made at once, or a reading can be made at the expiration of

15 or 20 minutes in dulplicate. The calculation of the percentage of citral content in the extract is made by placing the standard citral tube at the 30 mm. mark and adjusting the tube containing the extract under examination so that the 2 small discs of colour as observed through the two immersion tubes are similar in tint.

Kleber (*Amer. Perfumer*, 1912, 6, 284) uses a method based on the phenylhydrazine reaction, which, as slightly modified by Schimmel & Co., is as follows:

About 2 c.c. of oil are mixed with 10 c.c. of a freshly prepared 2% alcoholic phenylhydrazine solution, and allowed to remain undisturbed during 1 hour in a glass-stoppered flask of about 50 c.c. capacity. 20 c.c. of N/10 hydrochloric acid are then added and the liquid is mixed by gently moving the flask backwards and forwards. After adding 10 c.c. of benzene the mixture is shaken vigorously and poured into a separating funnel. The acid layer, amounting to about 30 c.c. which separates clearly after the mixture has been left to settle a short time, is then filtered on a small filter.

To 20 c.c. of this filtrate 10 drops of diethyl-orange solution (1: 2000) are added and the mixture is titrated with N/10 potassium hydroxide solution until a distinct yellow colour appears. From this the quantity in c.c. of N/10 potassium hydroxide solution required for 30 c.c. of the filtrate is calculated. For the purpose of estimating the value of the phenylhydrazine solution a blank test without oil is made in a similar manner. If it is found that the quantity of solution used up for 30 c.c. of the filtrate = $a$ in the first, and = $b$ in the second experiment, it follows that the quantity of citral present in the amount of oil under test ($s$ grm.) equals $a - b$ c.c. of N/10 solution. Hence, 1 c.c. N/10 potassium hydroxide being equal to 0.0152 grm. citral, the percentage proportion of citral in the oil is expressed by the following formula

$$\frac{(a - b) \cdot 1.52}{s}$$

The object of the extraction with benzene is to reclarify the solution, which becomes turbid after the addition of the hydrochloric acid. When this has been done it is easier to recognise the change in the colour during the titration.

The aldehydes of the closed chain series which are of importance commercially may now be dealt with.

## Benzaldehyde, $C_6H_5.COH$

The essential oils of the bitter almond, peach kernel and apricot kernel, consist, after removal of hydrocyanic acid, almost entirely of benzaldehyde. Artificial benzaldehyde is made on a very extensive scale, and has largely replaced the natural oil, frequently dishonestly.

Adulteration of the natural oil with the artificial product is usually impossible to detect, except when, as is very frequently the case, the artificial product contains traces of chlorine due to the process used in its manufacture.

The importance of obtaining benzaldehyde practically free from chlorine was originally only of importance because, when it was used for perfuming pale coloured soap, the soap became discoloured when chlorine was present. Today it is to be regretted that the principal demand for an absolutely chlorine-free product is due to the fact that the presence of even the minutest trace of chlorine reveals the fact that a so-called expensive natural oil is adulterated with, or even consists wholly of artificial benzaldehyde. Benzaldehyde has the following characters:

| | |
|---|---|
| B. p. | 180° |
| Sp. gr. at 15.5° | 1.052 |
| Opt. rot. | 0° |
| Ref. index at 20° | 1.5450 |

It yields a semicarbazone melting at 214°, and a phenylhydrazone melting at 156°. It rapidly oxidises, by exposure to the air, to benzoic acid, melting at 121°.

The detection of chlorine is the most important analytical process necessary in the examination of benzaldehyde. For detecting substantial amounts the following process has been recommended by Schimmel & Co.

A piece of filter paper about 2 inches by 1 inch is rolled up and saturated with the liquid. It is placed in a small porcelain dish, which rests in a larger dish. The paper is ignited and a large beaker with its inside moistened with distilled water is placed over it, with its rim resting in the outer dish. When the flame is extinguished, the beaker should be left in position for a minute, and then the beaker is washed out with a jet of distilled water, a drop of nitric acid added, the liquid filtered and tested for chlorides with silver nitrate solution. Combustion with pure lime will detect down to about

0.1% of chlorine.    Five grm. of pure lime and 1 c.c. of benzaldehyde are placed in a platinum crucible, more lime placed on the top, and the whole gently ignited.    The lime is dissolved in dilute nitric acid and tested for chlorine in the usual manner.

Salamon prefers the following method, which gives the most satisfactory results.    About 2 grm. of the benzaldehyde are heated in a retort with 40 c.c. of strong sulphuric acid, to which 5 c.c. of concentrated nitric acid are added.    The fumes are collected in a solution of silver nitrate and the silver chloride collected and weighed, precaution being taken to boil with dilute nitric acid to prevent silver sulphite or sulphate from being collected.

The heating should be very gradual, and no frothing should be allowed until the end of the operation.    This method will detect about 0.01% of chlorine.    Below this amount the indications are scarcely reliable.

Voigt (*Z. angew. Chem.*, 1922, **35**, 654) describes the following method for the estimation of chlorine in benzaldehyde, and similar volatile organic compounds.    From 10 to 20 grm. of the aldehyde are weighed into a lamp composed of a glass bulb arranged horizontally in an air bath which can be heated and connected with a combustion tube shaped like a pipette.    Hydrogen is passed through the lamp and carries over the benzaldehyde vapours; the outlet tube projects into the bulb of the combustion tube and ends in a burner nozzle formed by a quartz capillary.    The issuing hydrogen and benzaldehyde vapours are ignited and burn quietly in oxygen supplied to the combustion tube, until all the benzaldehyde has been vaporised.    The products of combustion are passed over 2–3 grm. of granular anhydrous sodium carbonate packed in the narrow part of the combustion tube and heated by gas burners, and the water formed is collected in a vessel containing calcium chloride.    About 7 grm. of benzaldehyde can be burned in an hour.    At the end of the combustion the soda is washed out into a beaker with dilute nitric acid and titrated with N/10 silver nitrate.    As little as 0.001% of chlorine can be estimated accurately by this method.    It should, however, be remembered that commercial hydrogen in cylinders contains a trace of chlorine which averages 0.003 grm. of chlorine per cubic metre.    This must be allowed for by approximately estimating the rate of flow of the hydrogen per hour, and applying the necessary correction.

## Salicylic Aldehyde, $C_6H_4(OH)(COH)$

This highly odorous aldehyde is found naturally in oil of Meadow-sweet and other varieties of *Spiræa*. It is also produced artificially by condensing phenol with chloroform with the aid of sodium hydroxide. It is a very fragrant oil having the characteristic odour of meadowsweet, and having the following characters:

Sp. gr. at 15.5°..................................... 1.170
B. p............................................... 197°
Solidifying point .................................. −20°

It yields an oxime melting at 57° and a phenylhydrazone melting at 96°.

## Cinnamic Aldehyde, $C_6H_5.CH:CH.CHO$

Cinnamic aldehyde forms the main constituent of cassia and cinnamon oils, and is also manufactured artificially on a considerable scale, being employed as the basis for the manufacture of artificial cinnamon oil. It is prepared by the condensation of benzaldehyde and acetaldehyde. It is an odorous oil having the following characters:

B. p............................................. 253°–254°
Sp. gr. at 15.5°.................................. 1.0560
Opt. rot......................................... 0°
Ref. index at 20° ................................ 1.6195

It yields a phenylhydrazone melting at 168° and a semicarbazone melting at 208°.

## Phenylacetic Aldehyde, $C_6H_5.CH_2CHO$

Phenylacetic aldehyde is a constituent of several essential oils, but owing to its comparatively high solubility it is to some extent dissolved out by the distillation waters and the resulting commercial oil lacks the powerful and characteristic odour which would otherwise be present. It possesses a very powerful odour of hyacinth, and, together with bromostyrolene, forms the basis of artificial hyacinth and narcissus perfumes. It is prepared artificially on a considerable scale and has the following characters:

B. p............................................. about 198°
Ref. index at 20° ................................ 1.5300
Sp. gr. at 15.5°.................................. about 1.060

## Anisic Aldehyde, $C_6H_4(CHO)(OCH_3)$

Although anisic aldehyde is found to a small extent naturally in essential oils, the commercial article is entirely an artificial product.

It results from the careful oxidation of anethol, the characteristic odorous constituent of aniseed oil. It has a very sweet and powerful odour and is known as "aubepine" or artificial hawthorn. It is used as the basis of all the perfumes of the hawthorn and "May blossom" type. Its characters are as follows:

```
B. p. .............................................. 246°
Sp. gr. at 15.5° ..................................... 1.1275
Opt. rot. ........................................... 0°
Ref. index at 20° ................................... 1.5730
```

It forms a semicarbazone melting at 203°–204°, and two oximes, one of which melts at 63° and the other at 132°.

The "solid" aubepine of commerce is the sodium disulphite derivative of anisic aldehyde.

## Vanillin, $C_6H_3(CHO)(OCH_3)(OH)$

Vanillin is the natural odorous and flavouring constituent of the vanilla bean and is made artificially from eugenol on a very large scale. It is also prepared from guaiacol to a certain extent. There are numerous methods for the manufacture of vanillin which need not be discussed here. The bulk of the commercial acticle is prepared by converting eugenol into isoeugenol by isomerisation with alkali hydroxide, then acetylating to form acet-isoeugenol, which is finally oxidised to vanillin. Whether prepared in this, the usual manner, or from guaiacol, the resulting vanillin should have identical characters.

If vanillin possesses a distinct odour of coal tar products it may be definitely rejected as being unfit for use, as it imparts a disagreeable odour to the chocolate or other substance it is used to flavour.

Vanillin forms fine white needles melting at 81°–82°, or sometimes when absolutely free from even traces of impurities (which is rarely the case) at a degree or so higher. It yields an oxime melting at 121°–122° and bromo-vanillin melting at 160°–161° when it is treated with bromine water.

Vanillin is not unfrequently adulterated with acetanilide or other neutral substances. The melting point will then be affected, and if

acetanilide be present the phenyl-isocyanate reaction is obtained by warming the sample with sodium hydroxide solution and chloroform, when the odour of phenyl-isocyanate is unmistakable. A quantitative examination should be made by dissolving a known weight in ether, and the liquid well shaken with a cold saturated solution of bisulphite. The bisulphite solution is separated, the ethereal liquid again extracted with bisulphite solution, washed twice with water, and the ether evaporated. If the vanillin be pure, there is practically no residue. If acetanilide be present it is weighed and its identity established by its m. p. (113°) and the phenyl isocyanate reaction.

Acet-eugenol or acet-isoeugenol is occasionally present as the result of careless manufacture. As this rapidly decomposes in the food stuff, liberating acetic acid, it is a very objectionable impurity. Pure vanillin gives a yellow colour when moistened with sulphuric acid. In the presence of the aceto compound a cherry red colour results. Benzoic acid is used as an adulterant. This is detected by the high acid value of the sample, and can be estimated in the same manner as acetanilide, care being taken to dry the residue at a very low temperature in a desiccator. The melting point and the usual ferric chloride reaction will serve to identify the residue as benzoic acid.

**Estimation of Vanillin in Vanilla Beans.**—Vanilla beans contain from about 1% of vanillin (poor grade Tahiti beans) up to 2.9% in the finest Bourbon vanilla. Twenty grm. of the pods are crushed with sand, and extracted with ether in a Soxhlet tube. The ethereal solution is extracted with sodium bisulphite solution. The separated solution is treated with dilute $H_2SO_4$, the $SO_2$ driven off by a current of $CO_2$, and the vanillin extracted with ether, the ethereal solution is washed with water, the ether driven off and the vanillin dried at a low temperature and weighed.

Hanus (*Pharm. Zeit.*, **50**, 1022, 157) recommends the following method. Three grm. of the well crushed pods are thoroughly extracted with ether in a Soxhlet tube, the solvent distilled off slowly, and the residue dissolved in a little perfectly dry ether, filtered and the ether cautiously driven off. The residue is dissolved in 50 c.c. of water at about 60° on a water bath, and 0.25 grm. of *meta*-nitrobenzaldehyde is then added to the solution and the mixture well shaken for a short time in a stoppered flask. It is then allowed to stand for 24 hours with occasional shaking. The vanillin is quantita-

tively precipitated as vanillin-*meta*-nitrobenzhydrazone. The precipitate is collected, allowed to dry in the air, washed with petroleum spirit to remove fat, then with water, again allowed to dry, and finally washed with petroleum ether dried and weighed. The weight, multiplied by 0.4829, gives the weight of vanillin present.

To estimate vanillin in domestic essence of vanilla, in which coumarin is also sometimes present, the method of Winton & Bailey, which is a modification of that of Hess & Prescott (*J. Amer. Chem. Soc.*, 1899, 256) is the most convenient. It also enables acetanilide to be estimated, which, if present, may be accepted as a positive indication of the presence of artificial vanillin. About 25 grm. of the sample are weighed into a beaker holding 200 c.c. and marked at 25 and 50 c.c. It is diluted to 50 c.c. with water and evaporated on a water bath to 25 c.c. at a temperature not exceeding 70°. It is again diluted to 50 c.c. with water, and again evaporated to 25 c.c. A solution of lead acetate is then added until no further precipitation takes place. The liquid is well stirred and filtered through moistened filter paper, and washed three times with hot water, so that the total filtrate is not more than 50 c.c. This, when cold, is shaken with 20 c.c. of ether in a separator. The ether is separated and the liquid again extracted three times with 5 c.c. of ether. The combined ether extracts are then shaken with 10 c.c. of a 2% solution of ammonia, and with three further portions of 5 c.c. each. The ethereal solution is reserved (B) and the combined ammoniacal extracts are slightly acidified with hydrochloric acid (10%), and then extracted with ether, the ether evaporated at a low temperature and finally in a desiccator and weighed (A). If acetanilide is absent this may be taken as pure vanillin and its melting point should not be lower than 79°. If acetanilide has been detected, the residue A should be dissolved in 15 c.c. of 10% ammonia and the liquid extracted twice with ether. The ether will leave a residue of acetanilide, which is deducted from A to give the vanillin. The ethereal solution, B, is evaporated at room temperature, dried in a desiccator and weighed. It is then extracted several times with petroleum ether, which is decanted each time. If the residue is completely dissolved it may be taken as pure coumarin, but any undissolved residue is probably acetanilide, which should be added to that found in the original residue A.

## Heliotropin, $C_8H_6O_3$

Heliotropin, or piperonal, is the methylene ether of protocate-chuic aldehyde. It occurs naturally in a number of plants, but not in sufficient quantity to extract it commercially. It is a powerful perfume, representing the heliotrope series of odours, and is manufactured on a considerable scale by isomerising safrol to isosafrol, and oxidising this with potassium permaganate or chromic acid.

Heliotropin forms white crystals, melting at $37°$. It yields a bromo-piperonal when treated with bromine in carbon bisulphide, melting at $129°$. The oxime exists in two isomeric forms, one melting at $111°$ and the other at $146°$. Its semicarbazone melts at $146°$. Compounds sold under names such as heliotropol, etc., are usually merely diluted heliotropin, he usual diluent being acetanilide.

## (F) KETONES

Compounds of ketonic functions occur in essential oils and are manufactured artificially for perfumery purposes to a very considerable extent. They may be divided into two groups—open-chain compounds, such as methyl-heptyl and methyl-nonyl ketones; and cyclic ketones, including the ionones, the camphor group, and the benzenoid ketones.

**Open-chain Ketones.**—In accordance with a general reaction, aldehydes and methyl-ketones may be isolated from essential oils by the action of sodium hydrogen sulphite. This separation is usually made after removing the free acids by shaking with sodium carbonate, and the esters by hydrolysing with alkali hydroxide. For estimating ketones, the oil, or a suitable fraction of it, is shaken with a concentrated solution of sodium hydrogen sulphite. This method does not always yield correct results, but is the most generally applicable. To isolate the ketone the crystalline compound $R_1R_2C(OH)SO_2$-ONa is washed with ether, drained, pressed, and decomposed with sodium hydroxide either alone or in presence of ether, and the ketone is then separated and purified by the ordinary methods.

To determine the amount of the ketone, the unabsorbed portion is measured in the graduated neck of a flask in the same manner as in the case of aldehydes.

## Methyl-amyl Ketone, $CH_3.CO.C_5H_{11}$

This substance is found in the essential oils of cloves and cinnamon. It has the following characters:

Sp. gr. at 15.5°.................................. 0.826
B. p. ............................................ 152°
M. p. of semicarbazone.......................... 122°–123°

### Ethyl-amyl Ketone, $C_2H_5.CO.C_5H_{11}$

This ketone has been isolated from lavender oil.   Its characters are as follows:

Sp. gr. at 15.5°.................................. 0.825
B. p. ............................................ 170°
Ref. index at 20° ................................ 1.4154
M. p. of semicarbazone............................ 117.5°

### Methyl-heptyl Ketone, $CH_3.CO.C_7H_{15}$

Methyl-heptyl ketone is found in attar of rose and, in very small amount in oil of cloves.   It has the following characters:

Sp. gr. at 15.5°.................................. 0.835
B. p. ............................................ 196°
M. p. ............................................ −17°
M. p. of semicarbazone.......................... 118°–119°

### Methyl-nonyl Ketone, $CH_3.CO.C_9H_{19}$

This ketone forms the major constituent of European oil of rue, of which it constitutes nearly 90%.   Thoms (*Ber. deut. pharm. Ges.*, 1901, **10**, 3) has shown that it is associated with about 5% of the heptyl ketone (*vide infra*).   The Algerian oil contains about 90% of these ketones, but in this case there is nearly twice as much of the lower as of the higher homologue.   Power and Lees (*Chem. Soc. Trans.*, 1902, **81**, 1585) found 80% of the two ketones in an oil apparently of Algerian origin.

The ketone boils at 232° under 760 m.m. pressure and has a sp. gr. 0.829.   The oxime, $C_9H_{11}C(CH_3):NOH$, melts at 46° and the *semicarbazone*, $C_9H_{11}C(CH_3):N.NH.CO.NH_2$, at 123°.   The enolic *benzoyl-derivative*, $C_8H_{17}CH:C(CH_3).O.CO.C_6H_5$, prepared by boiling the ketone with benzoyl chloride and distilling under reduced pressure, boils at 235° at 50 mm. and is immediately hydrolysed by warm dilute alcoholic potassium hydroxide.

### Methyl-n-heptyl Ketone, $CH_3.CO.C_7H_{15}$

This ketone boils at 195° under 763 mm. pressure and has sp. gr. 0.8296 at $\frac{14°}{16°}$.   The *semicarbazone* melts at 119° to 120°.   The enolic *benzoyl derivative* boils at 210° to 211° under 50 mm. pressure.

## Methyl-heptenone, $CH_3.C(CH_3):CH.CH_2.CH_2.CO.CH_3$

This unsaturated open-chain ketone is present to the extent of 1 to 4% in lemon-grass oil. For its extraction the fraction of the oil distilling at 180° should be agitated with a solution of sodium bisulphite in 1.5 parts of water. The ketone liberated from the solid bisulphite compound on treatment with sodium hydroxide is optically inactive, has a specific gravity 0.855 and a refractive index of 1.43805. It yields a semicarbazone, m. p. 136°–138°. Methyl-heptenone also results from the distillation of cineolic anhydride.

## Irone and the Ionones, $C_{13}H_{20}O$

The resemblance in odour of orris root and the violet flower is so marked, that when Tiemann and Kruger commenced their classic work on the synthesis of the violet odour, they considered it impossible to obtain sufficient of the substance they desired to investigate from the violet so they decided to work on the odorous constituent of orris root. In the result, they isolated a ketone which they termed irone, $C_{13}H_{20}O$. This substance has the following constitution:

$$
\begin{array}{c}
C(CH_3)_2 \\
HC\diagup\phantom{xx}\diagdown CH.CH:CH.CO.CH_3 \\
HC\diagdown\phantom{xx}\diagup CH.CH_3 \\
CH_2
\end{array}
$$
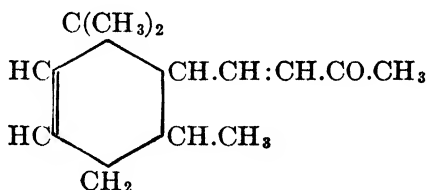
Irone has the following characters:

B. p. at 16 mm. ......................... 144°
Sp. gr. at 15.5°. ......................... 0.940
Ref. index at 20° ......................... 1.5011
Opt. rot. ................................. +40° approximately

It forms an oxime melting at 121°–122°, a *p*-bromphenylhydrazone melting at 174°–175°, and a thiosemicarbazone melting at 181°. It was Tiemann and Kruger's attempt to synthesize irone that led to the discovery of the closely allied isomeric substance, ionone, which is today an important commercial article, on which almost the whole of the violet-perfume industry is based.

Citral was condensed with acetone, with the result that a ketone isomeric with irone was obtained:

$$C_{10}H_{16}O + (CH_3)_2CO = C_{13}H_{20}O + H_2O$$

This ketone was termed *pseudo*-ionone. It is a liquid of sp. gr. 0.898 and ref. ind. 1.5335.

*Pseudo*-ionone was heated with dilute acids in the presence of a little glycerine, and was found to be isomerised into a different ketone, which was termed ionone. This substance, long believed to be a single substance, is now known to be a mixture of two compounds, known as $\alpha$-ionone and $\beta$-ionone.

Today there are numerous commercial articles sold as artificial violet perfumes. All of these are based on ionone or a homologue of ionone, and all of which have a pronounced odour of violets, together with a suggestion of vine leaves. Commercial "ionone" is usually the reaction mixture of the isomeric $\alpha$- and $\beta$-ionones; the isomers are also sold in a pure condition, and it has been found that $\alpha$-ionone has the sweeter and more penetrating odour, resembling orris more than violets, whilst $\beta$-ionone more closely resembles the true violet flower perfume.

Commercial ionone should always be a 100% article, and not a diluted substance. It has the following approximate characters:

B. p. at 10 mm. ............................ 126°–128°
Sp. gr. at 15.5°. ........................... 0.935 to 0.940
Ref. ind. at 20° ........................... 1.5030 to 1.5070
Opt. rot. ................................. 0°

$\alpha$-ionone and $\beta$-ionone have the following characters:

|  | $\alpha$-IONONE | $\beta$-IONONE |
| --- | --- | --- |
| Sp. gr. at 15.5°. | 0.934 | 0.949 |
| Ref. ind. at 20° | 1.4990 | 1.5198 |
| B. p. at 12 mm. | 127°–128° | 134°–135° |
| M. p. of oxime | 89°–90° |  |
| M. p. of semicarbazone | 107° | 148°–149° |
| M. p. of bromphenylhydrazone | 142°–143° | 116°–118° |

The most effectual method for the separation of the two isomeric ionones is that of Chuit. The predominating constituent of the commercial ionone is $\alpha$-ionone, but if cold concentrated sulphuric acid be used as the condensing agent, $\beta$-ionone is found in much greater quantity. The method of separation of the isomers is based on the relative insolubility of the sodium salt of the hydrosulphonic compound of $\alpha$-ionone, whilst the corresponding $\beta$-ionone compound is soluble. If sodium chloride be added to the hot solution of the hydrosulphonic compounds, separation of the $\alpha$-salt soon takes place

as the solution cools. The salt crystallises in fine white scales, and is recrystallised from hot water. The $\beta$-salt remains in solution. The salts are decomposed by sodium hydroxide solution and the liberated ionones recovered by steam distillation. The constitutions of the two isomers are as follows:
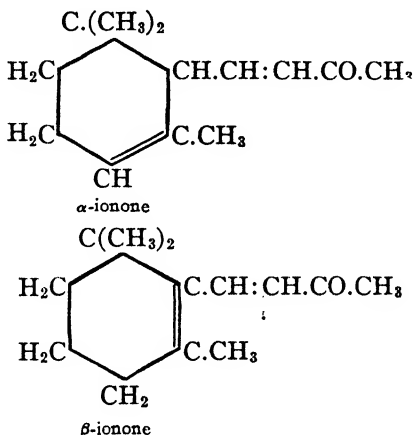


$\alpha$-ionone



$\beta$-ionone

The enormous demand for violet perfume has led to the development of the ionone industry on a very large scale. This, in its turn, has largely extended the distillation of lemon-grass oil, from which the citral is obtained. There is very little purely natural violet perfume sold to the public. Most of the violet extracts and essences are purely artificial, made from ionone or its homologues, but a few of them contain a small amount of true violet perfume, which is obtained from the flowers in the south of France in the form of a pomade, and which is then fortified with a little ionone.

## Cyclic Ketones

The cyclic ketones are for the most part closely related to the terpenes, and, like them, most of them contain 10 carbon atoms in the molecule. That this relationship is fundamental and not merely superficial is shown by the fact that camphor is now prepared artificially on a considerable scale from turpentine, and may in its turn be converted into camphene, another member of the terpene group.

## Piperitone, $C_{11}H_{11}O$

Piperitone is a ketone which is of great importance on account of recent developments in the manufacture of thymol artificially for which it may become raw a material of value. It was first obtained from the essential oil of *Eucalyptus dives* by Baker and Smith, and has since been obtained to the extent of 80% from the Indian essential oil from *Andropogon iwarancusa*, by Simonsen (*J. Chem. Soc.*, 1921, 1644).

Penfold, who has made an exhaustive study of piperitone, considers that it has the following constitution:

$$C.CH_3$$
$$H_2C \diagup \diagdown CH$$
$$H_2C \diagdown \diagup CO$$
$$C.CH.(CH_3)_2$$
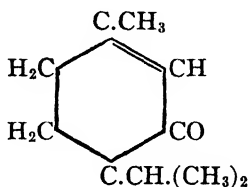
He considers that it is identical with

(1) Wallach's synthetic △-menthenone—3.

(2) The ketone isolated by Schimmel from Japanese peppermint oil (*Semi-annual Report, Oct.*, 1910, 97).

(3) The ketone isolated from camphor oil, of this composition.

(4) The △-menthenone found in oil of *Cymbopogon sennaarensis*.

Simonsen (*loc. cit.*) also considers that piperitone is identical with △-menthenone-3, but Read and Smith (*J. Chem. Soc.*, 1921, 779) consider that the two ketones are not identical.

Piperitone is prepared by fractional distillation of the oil of *Eucalyptus dives*, and purified by means of its sodium bisulphite compound. When pure it has the following characters:

| | |
|---|---|
| B. p. | 235° |
| B. p. | 106°–108° at 10 mm. |
| Sp. gr. at 15.5° | 0.9393 |
| Opt. rot. | variable, up to −50° |
| Ref. index at 20° | 1.4837 |
| Oxime | melts at 117°–118° |
| Oxamino-oxime | melts at 169°–170° |
| Semicarbazone α | melts at 225°–226° |
| Semicarbazone β | melts at 175°–176° |
| Semicarbazone β (racemic) | melts at 188°–189° |
| Benzylidene derivative | melts at 61° |
| Bis-nitroso compound | melts at 96°–97° |

It yields menthol and other products on reduction with sodium in moist ether, and menthone when reduced with hyrogen in the presence of nickel. On oxidation with ferric chloride it yields thymol, and with potassium permanganate, diosphenol. To detect piperitone in essential oils, 1 c.c. of the oil is mixed with 1 c.c. of alcohol and 4 c.c. of ether. One grm. of sodium amalgam is then added. If piperitone is present a reddish brown coloration is at once produced, and at the end of about ten minutes a copious white crystalline precipitate separates. This substance is a pinacone, which can be filtered off, washed with ether, dried, recrystallised from boiling alcohol, and its melting point determined. It consists of two individuals melting at 135°–136°, and 166°–167° respectively, but the substance so separated is found to melt at between 142° and 149°.

Piperitone can be quantitatively determined by the neutral sodium sulphite absorption process, care being taken that the water bath should be vigorously boiling and that the flask is kept constantly shaken.

## Verbenone, $C_{10}H_{14}O$

Verbenone is a ketone occurring naturally in the true oil of verbena (*i. e.*, not in lemon-grass oil). Its characters are as follows:

B. p. ........................................... 227°–228°
Sp. gr. at 15.5°.................................. 0.981
Opt. rot. ....................................... +61° 20′
M. p. ........................................... +6.5°
Ref. index at 20° ............................... 1.4993

Its constitution is
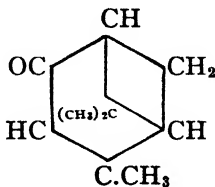


## Acetophenone, $C_6H_5.CO.CH_3$

Acetophenone is an aromatic ketone occurring in oil of Labdanum, and also in the oil of *Stirlingia latifolia*, of which it forms about 90% or more. It is used in medicine as a hypnotic and also in perfumery. It is, as found in commerce, always manufactured artificially, by, for

example, condensing benzene and acetyl chloride in the presence of aluminium chloride. It is a crystalline solid, melting at 20° and boiling at 200°–202°. Commercial samples are, however, almost invariably liquid, as the merest trace of impurities inhibits crystallisation. Its methyl derivative, methyl-acetophenone $CH_3.C_6H_4.-CO.CH_3$, is prepared in a similar manner, substituting toluene for benzene. It is an oil of powerful floral odour b. p. 220°, sp. gr. 1.006. Acetophenone forms an oxime melting at 56°–60° and a semicarbazone melting at 185°–187°. Methyl-acetophenone forms an oxime melting at 88° and a phenylhydrazone melting at 97°.

### Jasmone, $C_{11}H_{16}O$

Jasmone is a ketone isolated from the essential oils of jasmin and neroli. Its odour is that of jasmin, and it has the following characters:

| | |
|---|---|
| Sp. gr. at 15.5° | 0.945 |
| B. p. | 257°–258° |
| M. p. of oxime | 45° |
| M. p. of semicarbazone | 201°–204° |

### Muskone and Zibethone

Muskone is a ketone which has been isolated from natural musk, in which it is present to the extent of from 0.5 to 2%. It is a viscous colourless oil having an intense musk odour. It boils at 327°–330°, yields an oxime melting at 46° and a semicarbazone melting at 133°–134°.

Zibethone, $C_{17}H_{30}O$ is a ketone isolated by Sack (*Chem. Soc. Trans.*, 1915, **107**, 314) from civet. Its odour is that of civet, and it has the following characters:

| | |
|---|---|
| B. p. | 205° at 17 mm. |
| B. p. | 342° at 741 mm. |
| M. p. | 32.5° |
| M. p. of oxime | 92° |
| M. p. of semicarbazone | 187° |

### Camphor, $C_{10}H_{16}O$

**Origin.**—Common or Japan camphor occurs in minute crystals in the wood of the camphor-laurel (*Laurus* or *Cinnamomum camphora*) and is extracted by distilling the chopped-up branches of the tree with water.

The crude camphor thus obtained is exported from Japan and Formosa, and to a limited extent from China, and is refined in Europe by

mixing it with a small proportion of lime or charcoal and subliming it in large glass vessels called "bombolas," or by subliming it from iron retorts into a cooled chamber, where it condenses in the form of flowers of camphor. It is subsequently pressed into transparent cakes by hydraulic power. Camphor also occurs in the oils of sage, lavender, spike-lavender, and rosemary.

It can also be prepared by oxidising the secondary alcohol borneol, $C_{10}H_{18}O$, which is exported on a considerable scale from Borneo and Sumatra under the name of Borneo camphor. This method of preparation has acquired great importance in recent years as the last stage in the manufacture of camphor from turpentine.

The first stage in the process consists in passing dry hydrogen chloride into well-cooled and carefully dried turpentine, when pinene hydrochloride, $C_{10}H_{17}Cl$, is thrown down as a white crystalline mass. The hydrochloride resembles camphor somewhat closely and was at one time known under the misleading title of artificial camphor. It can, however, be readily distinguished by using the ordinary tests for halogens; thus, if a copper wire be heated in the flame of a Bunsen burner until it no longer produces a coloration, an intense green tint is developed by dipping the wire into the fictitious "camphor" and again heating it in the flame; no such coloration is produced by natural camphor, nor by genuine camphor prepared artificially from turpentine as described below, if the later steps in the manufacture have been efficiently carried out.

The second stage in the preparation of the true artificial camphor consists in the removal of hydrochloric acid from the pinene hydrochloride, and the production of iso-bornyl acetate either directly in one process or indirectly with separation of camphene as an intermediate product. In the latter case the removal of the hydrogen chloride is effected by means of (a) ammonia or organic bases or (b) alkalies in the free state, or in combination with a weak acid, as in the form of soap; the camphene is then converted into iso-bornyl acetate by heating with glacial acetic acid containing about 5% of sulphuric acid.

$$C_{10}H_{17}Cl = C_{10}H_{16} + HCl$$
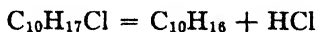
Pinene hydro-     Camphene
chloride

$$C_{10}H_{16} + CH_3.CO.OH = C_{10}H_{17}.O.CO.CH_3.$$
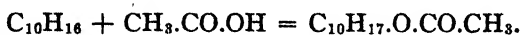
Camphene                    Isobornyl acetate

A direct conversion into the acetate can be effected by heating the hydrochloride with glacial acetic acid together with 5 to 10% of zinc chloride (Weizmann, B. A. Report, Dublin, 1908, p. 661). The acetate is hydrolysed by boiling with alcoholic sodium hydroxide, the alcohol distilled off, and the borneol, which separates in white crystals is oxidised by means of (e. g.) nitric or chromic acid to camphor. It is important that no unchanged hydrochloride should be left in the finished product, as a small proportion of chlorine is sufficient to render the material useless for the manufacture of celluloid, and undesirable for many other purposes. When properly prepared, however, artificial camphor resembles the natural product in all its essential properties and differs from it only in the absence of optical activity.

Camphor is known commercially in two forms—as "flowers" of camphor, in the form of small crystals obtained by subliming the camphor in a chamber; and in semi-transparent blocks, prepared from the flowers by compression. By slow sublimation at atmospheric temperatures it is obtained in brilliant crystals belonging to the hexagonal system. Such crystals are often found deposited on the sides of the bottles in which it is preserved. It vaporises readily, when exposed to the air, and sublimes without residue when heated. When partially enclosed so as to check the rapidity of vaporisation, it melts at 176°–177° and boils without decomposition at 204°. It is readily inflammable and burns with a smoky flame.

Camphor is somewhat lighter than water, the sp. gr. being given variously from 0.980 to 0.996. When thrown on the surface of clean water, camphor goes through rapid whirling movements, which are arrested by the addition of a drop of oil.

Its solubility in water is very slight, amounting to only about 1 part in 1000, but it is freely soluble in all organic liquids. It dissolves in less than its own weight of alcohol (120:100) of 0.806 sp. gr., and is readily soluble in ether, chloroform, acetone, glacial acetic acid, carbon disulphide, and fixed oils. A saturated solution of camphor in olive oil contains 27% by weight of camphor. Its solubility in water is only slightly affected by the addition of small amounts of acid or alkali, but it dissolves readily in concentrated hydrochloric, hydrobromic, and sulphuric acids. The solid camphor possesses the property of absorbing gaseous hydrogen chloride, nitrogen peroxide, and sulphur dioxide, forming liquids which are

decomposed by the addition of water. The compound of camphor with sulphur dioxide has been proposed as a disinfectant under the name of "Thiocamph." Camphor also liquefies when triturated or heated with menthol, thymol, phenol or chloral hydrate; the products, which appear to be definite compounds, have received a limited application in medicine.

Ordinary camphor is dextrorotatory.

The essential oil obtained by distillation from the leaves of fever-few (*Matricaria parthenium*) contains a variety of camphor agreeing in all respects with that obtained from the camphor-tree except that it possesses a lævoration equal to the dextrorotation of the latter kind. By mixing these two varieties of camphor in equal proportions, a *racemic camphor* is obtained which is optically inactive and is identical with the camphor prepared from turpentine. This inactive camphor has m. p. 179°, and yields derivatives which differ in their solubilities and m. p. from the parallel products obtained from ordinary camphor. (See A. Haller, *Compt. rend.*, 1887, **105**, 66.)

The specific rotation of camphor varies considerably with the nature of the solvent and the concentration of the solution. Landolt gives the formula

$$[\alpha]_D = +55.4 - a.q,$$

where $q$ is the number of grm. of solvent in 100 grm. of solution. The value of $a$ varies with the solvent, being 0.1372 for alcohol and 0.1632 for benzene. Thus the apparent specific rotation power of a solution of 10 grm. of camphor in 90 grm. of alcohol will be:

$$55.4° - 12.3° = + 43.1°$$

From the observations of Partheil and van Haaren (*J. Soc. Chem. Ind.*, 1900, **19**, 684) it appears that the more dilute the alcohol, the lower the apparent specific rotation of the dissolved camphor. Hence the amount of the latter cannot be accurately deduced from the observed rotation, unless the strength of the alcohol be also known. Further, when the solvent is kept of constant strength the specific rotation decreases slightly as the percentage of camphor increases. Partheil and van Haaren propose the formula: $P = 1.5152$ $a$, where P is the percentage of camphor by weight and $a$ the observed rotation for 200 mm. To ascertain the specific gravity of the alcohol used (S), they propose the following formula:

$$S = \frac{100 - p}{\frac{100}{d} - 1.05\,p}$$ ; where $p$ is the percentage of camphor by weight

and $d$ the specific gravity of the camphorated spirit.    Partheil and van Haaren give the following table:

| No. | Sp. gr. of alcohol | Camphor, % | Observed rotation, 200 mm. | Sp. rot., $[a]_D$ |
|---|---|---|---|---|
| 1 | 0.7896 | 10 | 6.98° | 43.4362 |
| 2 | 0.8212 | 10 | 6.78° | 40.6666 |
| 3 | 0.8505 | 10 | 6.69° | 39.0439 |
| 4 | 0.8637 | 10 | 6.65° | 38.1439 |
| 5 | 0.8781 | 10 | 6.60° | 37.2755 |
| 6 | 0.8909 | 10 | 6.59° | 36.7622 |
| 7 | 0.9007 | 10 | 6.59° | 36.4008 |
| 1 | 0.7895 | 8.37 | 5.79° | 43.2142 |
| 2 | 0.7895 | 6.81 | 4.69° | 43.1411 |
| 3 | 0.9007 | 8.35 | 5.48° | 36.2929 |
| 4 | 0.9007 | 6.82 | 4.40° | 35.6951 |

The following determinations of the specific rotation of camphor when dissolved in fixed oils are by P. Chabot (*Compt. rend.*, 1890, **3,**

| | Olive oil | Almond oil | Grape-seed oil |
|---|---|---|---|
| $[a]_D$ in 3% solution............ | 55.7° | 56.8° | 54.4° |
| $[a]_D$ in 20% solution........... | 55.2° | 54.3° | 54.3° |

231): From these results it appears that the value of $[a]_D$ varies little, but somewhat increases, with the dilution, whereas the reverse is the case with solutions of camphor in alcohol and benzene.

Camphor has a peculiar fragrant odour and somewhat bitter, burning taste, followed by a sensation of cold.   It has distinct, but not very powerful, antiseptic properties, and is inimical to insect life.   Hence its employment for preserving animal specimens in museums, etc.

It is extensively employed in medicine, both internally and externally.   In large doses it is distinctly poisonous, the most marked symptoms being cardiac depression, lividity of countenance, convulsions, stupor, retention of urine, and, in extreme cases, collapse.

When ingested by the dog, camphor appears in the urine as *campho-glycuronic acid*, $C_{16}H_{24}O_6$, which when boiled with dilute hydrochloric acid yields *camphoral*, $C_{10}H_{16}O_2$, a substance which crystallises in thin tablets, m. p. 197° to 198°, sublimes readily, and yields camphoric acid on oxidation.

The three chief pharmaceutical preparations of camphor are as follows:

**Camphor water** is a 0.1% solution of camphor, and is directed to be prepared by dissolving 1 part by weight of camphor in sufficient alcohol (90%) to form 3 volumes, and then pouring the solution gradually with shaking into 1000 parts of water, the liquid being occasionally shaken until the camphor is dissolved. The solution has an extensive use in medicine. The United States Pharmacopœia (8th Rev., 1900) preparation is apparently stronger, as it is made by rubbing up 8 grm. of camphor in 8 c.c. of alcohol with 15 grm. of purified talc; and after most of the alcohol has evaporated spontaneously distilled water is gradually added. The total volume is 1000 c.c. The mixture is filtered on a well-wetted filter.

**Spirit of camphor** is a solution of 1 part of camphor in 9 of 90% alcohol. The corresponding preparation of the United States Pharmacopœia (8th Rev.) is made by dissolving 100 grm. of camphor in sufficient alcohol to form 1000 c.c. Such a solution occupies fully the volume of the spirit used *plus* that of the camphor before solution, there being slight expansion rather than contraction in the process of solution. Rubini's "Essence of Camphor" (*Spiritus camphoræ fortior*) is a solution of camphor in an equal weight of rectified spirit.

On diluting an alcoholic solution of camphor with water, the solid is precipitated in white flocks. If the proportion of alcohol exceeds a certain limit, no amount of dilution will effect precipitation of the camphor.

**Liniment of camphor or camphorated oil, B. P.,** is a solution of 1 part by weight of camphor (in flowers) in 4 parts by volume of olive oil. Hence the preparation, when properly made, contains almost exactly 21% by weight of camphor.

In addition to the official preparations of camphor and the camphor derivatives, there are mixtures of camphor used in medicine (Coblentz, Newer Remedies, 4th ed., 1908, p. 29). Camphor, phenylated, is made by melting together equal parts of camphor and phenol.

There are also compounds of a similar nature in which salicylic acid, resorcinol, thymol, etc., are melted with camphor.

In addition to its employment in medicine, camphor is used extensively for the manufacture of the nitrocellulose products known as *Celluloid, Xylonite* and *Pyralin,* and is, or was, an ingredient of some varieties of blasting gelatin and smokeless powder.

Crude camphor as imported into this country arrives in tinned iron containers, and may contain as much as 10% of impurities. These consist of dirt, water, and camphor oil. As the liquid portion, if present in any quantity, settles to the bottom of the container, considerable care must be taken in the sampling.

The method of analysis is as follows:

*Dirt and Non-volatile Matter.*—From 2 to 3 grm. is volatilised in a tared glass dish at a considerable distance over a rose burner. If a water bath be used, the time of volatilisation is prolonged. The non-volatile matter is returned as "dirt and non-volatile matter."

*Water.*—About 10 grm. is centrifuged in a tube with a graduated capillary, with water-saturated benzene or petrol. For details of the apparatus used the original paper by Lane and Lubatti should be consulted (*vide Analyst,* 1920, **45,** 220).

*Oil.*—100 grm. are pressed in a strong press between fine lint. The loss in weight is calculated as oil and moisture. Or the oil may be approximately deduced from the melting point of the sample. It is probable that commercial camphor of the usual highest standard of purity rarely melts at a higher temperature than 175°.

As an example of a test of this nature carried out in the Sadtler & Son, Inc. laboratory, a sample of camphor melting at 160° was to be compared with known mixtures, and the following series of standards were made.

| Oil, % | Camphor, % | M. p. |
|:------:|:----------:|:-----:|
| 0 | 100 | 175 |
| 1 | 99 | 173 |
| 2 | 98 | 171 |
| 3 | 97 | 169 |
| 4 | 96 | 167.5 |
| 5 | 95 | 166 |
| 6 | 94 | 164.5 |
| 7 | 93 | 163 |
| 8 | 92 | 161.5 |
| 9 | 91 | 160 |

The sample in question was considered as having 9% of oil as its m. p. was 160°.

The iodine value also affords some indications as to the amount of oil present, as that of pure sublimed camphor does not exceed 1.5, whilst that of an average camphor oil is 130.

If chlorides are found, by ignition in a hard glass tube with pure quicklime and testing for chlorides in the usual manner, artificial camphor is present. This will be confirmed by the optical rotation, since artificial camphor is optically inactive. Stearic acid should be looked for. This will show a high acid value, and will of course, be present in the non-volatile matter. K. W. Lane gives the following typical analyses of a number of samples of crude camphor (*J. Soc. of Chem. Ind.*, through *Perfumery and Ess. Oil Record*, 1922, March, 81).

| No. | Dirt | Water | Oil (a) | Oil (b) | Camphor | Rotation | Sp. gr. (del.) |
|---|---|---|---|---|---|---|---|
| 1 | 0.14 | nil | ....... | 3.0 | 96.9 | 7.90 | 0.8134 |
| 2 | 0.10 | 6.4 | ....... | 1.0 | 92.5 | 7.57 | 0.8134 |
| 3 | 0.11 | 5 2 | ....... | 4.0 | 90.7 | 7.42 | 0.8134 |
| 4 | 0.12 | 7 4 | ....... | 4.0 | 88.5 | 7.45 | 0.8146 |
| 5 | 0.40 | 2.6 | ....... | 4.0 | 93.0 | 7.56 | 0.8146 |
| 6 | 0.10 | 9.0 | ....... | 1.0 | 89.9 | 6.70 | 0.8146 |
| 7 | 0.11 | 7.0 | ....... | 10.0 | 82.9 | 7.10 | 0.8146 |
| 8 | 0.36 | 6.8 | 4.0 | 6.0 | 87.8 | 7.48 | 0.8146 |
| 9 | 0.13 | 8.0 | 3.2 | 2.0 | 89.3 | 7.53 | 0.8146 |
| 10 | 0.22 | 5.7 | 2.0 | 3.0 | 91.6 | 7.88 | 0.8146 |
| 11 | 0.15 | 7.0 | 2.8 | 3.0 | 90.0 | 7.85 | 0.8146 |
| 12 | 0.12 | 4.5 | ....... | Trace | 95.4 | 7.98 | 0.8146 |
| 13 | 0.13 | 3.1 | 4.6 | 4.0 | 92.3 | 7.72 | 0.8146 |
| 14 | 0.12 | 0.6 | ....... | 1.0 | 98.3 | 8.10 | 0.8146 |
| 15 | 0.20 | 2.8 | 1.7 | 2.0 | 95.2 | 7.55 | 0.8334 |
| 16 | 0.08 | 0.5 | ....... | 1.5 | 97.9 | 7.92 | 0.8334 |
| 17 | 0.01 | nil | ....... | nil | 99.9 | 8.23 | 0.8290 |

*Notes.*—The camphor figure is found by difference. When more than one oil figure is available the average is used. The rotations are observed in a solution of 10 g. in alcohol, the density of which is given in the next column. It will be seen at once that the figures, even for the same alcohol, do not enable the camphor content to be deduced.

Camphor can be readily separated from non-volatile substances by distilling the mixture in a current of steam, but its accurate estimation in the presence of other volatile compounds presents some difficulty. The proportion of camphor present in camphor liniment and similar preparations can be ascertained with considerable accuracy by the direct observation of the optical activity of the liquid.

The following figures by N. Leonard and H. M. Smith (*Analyst*, 1900, **25**, 202) show the optical activity of solutions of various strengths of camphor in olive oil. Line 4 in the table shows the observed angular rotation of the solution in a 200 mm. tube. Line 5 shows the calculated angular rotation for 1% of dissolved camphor. These latter figures are corrected for the small rotation of olive oil itself, which, according to Bishop (*J. Soc. Chem. Ind.*, 1887, **6**, 750), is $+0.13°$ for 200 mm. Line 6, which has been added by Allen, shows the apparent sp. rot. of camphor calculated from Leonard and Smith's data.

| | A | B | C | D |
|---|---|---|---|---|
| 1. Dissolved camphor, % | 5.32 | 11.26 | 20.66 | 26.78 |
| 2. Sp. gr. at 60° F | 0.91903 | 0.92173 | 0.92604 | 0.92911 |
| 3. Rise of sp. gr. for 1 % camphor | 0.000446 | 0.000450 | 0.000454 | 0.000465 |
| 4. Angular rotation per 200 mm | 5.26° | 11.35° | 20.74° | 26.79° |
| 5. Angular rotation for 1 % camphor | 0.964° | 0.998° | 0.998° | 0.996° |
| 6. Apparent sp. rot. of dissolved camphor | 52.4° | 54.0° | 53.9° | 53.6° |

D was a saturated solution prepared by gently warming olive oil with excess of camphor, cooling to about 10° and filtering. The contained camphor was then ascertained from the loss of weight sustained on heating a portion of the solution at 110° to 120°.

It will be seen from these results that the rotation of the liquid is increased by nearly 1° for each unit % of camphor present, and that the observed angular rotation of a sample of camphorated oil in a 200 mm. tube gives at once, without calculation, the percentage of camphor with sufficient accuracy for most purposes. The rotation appears not to be appreciably influenced by ordinary variations of temperature.

Leonard and Smith found the rotation of two specimens of rape oil to be $-0.16°$ and $-0.3°$, and of sesame oil $+1.6°$, per 200 mm., results which are in accord with those of Bishop, while two samples of fluorescent mineral oil gave them rotations of $+0.12°$ and $+0.42°$. Experiments with rape oil and mineral oil showed, however, that the increased rotation caused by the solution of camphor in these oils is practically the same as with olive oil, so that if the nature of the oil used in the preparation of the sample is known, the process is still applicable. For the identification of the oil used, they found that the sample could be examined directly with the refractometer,

the refractive index of the oil being apparently almost unaffected by the presence of dissolved camphor.

For the gravimetric estimation of camphor in camphor liniment, 5 grm. of the sample should be heated in a shallow capsule to 120° for about 2 hours, when the loss of weight will be that of the camphor volatilised.[1] Or a good plan is to heat the liquid in a capsule over a water-bath, when the greater portion of the camphor will readily be volatilised and the remainder can be removed in the air-bath as before. The same method will give fairly good results with samples containing heavy mineral oil, but in the case of a more volatile fraction of petroleum being present the loss of weight will, of course, not be due solely to the camphor. F. Foerster drives a current of open steam through the oil, and when the distillate amounts to about 300 c.c. redistils it with the addition of a little alkali and a spiral of platinum wire to prevent bumping. The distillate is agitated with benzene and the amount of camphor deduced from the optical activity of the liquid.

F. Foerster (*Ber.*, 1890, **23**, 2981) employs a similar process for the estimation of the camphor in celluloid, xylonite, ivorine, and similar preparations. For this purpose, a quantity of the sample containing from 2 to 3 grm. of camphor is treated in a flask furnished with a condenser and tap-funnel with sufficient of a 10% solution of sodium hydroxide to saponify the substance. The flask is heated to about 80° till saponification is complete, when sufficient concentrated alkali is added to raise the strength of the liquid in the flask to about 10% of NaOH. The contents of the flask are then diluted, if necessary, to about 250 c.c., and distilled till about half the volume has passed over. The condenser should be connected air-tight upon the receiver, which should have a second orifice fitted with a U-tube containing an exact measure of benzene, to catch any uncondensed camphor-vapour.[2] When the distillation is complete, this benzene is added to the contents of the condenser, and more added to bring the total volume employed to 25 c.c. The contents of the receiver are then agitated to dissolve the camphor in the benzene, the latter

[1] Some samples of olive oil appear to gain slightly in weight on heating, while others lose weight. (See A. W. Nunn, *Pharm. Journ.*, 1902, **69**, 106.) It has been proposed to make a correction for this change, but this refinement is unnecessary.

An indirect method of estimating camphor in the liniment (in the absence of mineral oil) consists in applying Kœttstorfer's saponification process. The weight of potassium hydroxide (KOH) required for the saponification, multiplied by 5, gives the weight of fatty oil present in the portion of the sample operated on. 5 grm. is a suitable quantity of oil to employ. The results are satisfactory.

[2] Foerster uses a special form of receiver.

separated from the water, brought to a temperature of 20°, and the optical activity observed with a polarimeter. According to Foerster, the specific rotation of camphor in benzene solution is $+39.755° +$ $0.17254\ t$, whence $[a]_D = +40.11°$ at 20°. (Compare Landolt's formula *supra*.)

From *alcohol*, camphor may be partially separated by addition of water (see above), the solution being afterwards fractionally distilled. Or the camphor may be extracted from the largely diluted liquid by agitating it with a known weight or measure of a heavy petroleum fraction, and its amount deduced from the increased weight or volume of the separated solvent. O. Schmatolla agitates 10 grm. of the spirit in a burette with about 30 c.c. of a saturated solution of common salt, and dissolves the precipitated camphor by adding exactly 1 c.c. of a petroleum oil and gently rotating the burette. The increase of volume of the petroleum is noted, each 1.02 c.c. representing 1 grm. of camphor.

When the proportion of camphor in an alcoholic solution is roughly known, the amount may be deduced from the optical activity of the liquid, but the result will be only approximate unless the strength of the alcohol be also known.

The following process is given by E. Deussen (*Arch. Pharm.*, 1909, **247**, 307) for the *estimation of camphor in spirits of camphor*. Five grm. of the spirit of camphor are weighed into a tared 50 c.c. Erlenmeyer flask and 20 grm. of cold saturated ammonium sulphate solution and 30 grm. of water added. After well shaking the mixture is set aside in an ice-chamber for 12 hours. The separated camphor is drained and aggregated into a ball by means of a nickel spatula. The filter is covered with a watch-glass and another small watch-glass and a piece of card about the size of a post-card are tared. The camphor is spread out thinly with the nickel spatula on a porous tile, covered for some minutes with a watch-glass, and then transferred as completely as possible to the tared card, covered with the tared watch-glass and weighed. The amount of camphor found by this process is within 4 to 6 per cent. of the actual amount present.

The following process is proposed by F. W. Richardson and W. Walton (*Analyst*, 1908, **33**, 463–466) for the analysis of camphorated oil in order to detect and estimate artificial camphor, oil of turpentine, and essential oil of camphor, any or all of which may be present in

addition to natural camphor. 10 c.c. of the camphorated oil are placed in a small retort, and heated to a temperature of 200° by means of an oil-bath; a current of dry carbon dioxide is passed through the retort during the heating, and the neck of the retort is connected with a weighed, two-necked Woulff's bottle. A weighed, small spiral glass condenser is fitted in the second hole of this bottle. The volatile substances collecting in the neck of the retort, the Woulff's bottle, and condenser are weighed (the neck of the retort being cut off for this purpose), dissolved in carbon tetrachloride, and the solutions are united. This solution is weighed, and portions are used for the estimation of the sp. gr., iodine number, and polymerisation with sulphuric acid. The last-mentioned process is carried out by treating a weighed portion of the solution (about $\frac{1}{2}$) with $\frac{1}{3}$ of its volume of sulphuric acid, sp. gr. 1.84, the acid being added slowly and the mixture cooled. The latter is then distilled in steam, and the carbon tetrachloride solution separated from the distillate and weighed; the change in sp. gr. and ref. index of the solution enables the weight of the total camphors to be calculated, while the polarimetric reading in a 200 mm. tube, multiplied by 0.22385 and divided by 0.95, gives the amount of natural camphor. This, deducted from the total camphors, leaves the quantity of artificial camphor. When the amounts of the two camphors are known, the iodine number due to turpentine and oil of camphor enables the % of the last-named substances to be calculated. The following iodine numbers are assumed in the calculation: natural camphor, 5; artificial camphor, 7; essential oil of camphor, 190; and oil of turpentine, 370. These values are not correct; pure natural and artificial camphor rarely exceeds 2, and the oil of camphor associated with the camphor rarely exceeds 130.

Lohrmann (*Ber. deutsch. Pharm. Ges.*, 1909, **19,** 222) discusses the points of difference by which natural and artificial camphors are distinguished. The optical rotation in alcoholic solution is preferred as a means of estimating the amount of natural camphor in presence of artificial camphor. The importance in the celluloid industry of having artificial camphor free from chlorine is emphasized. Borneol and isoborneol are readily estimated in artificial camphor by the acetylation method. The melting point affords a useful indication of the purity of artificial camphor. For

celluloid manufacture the camphor should be free from traces of acid and the ash should in no case exceed o.o2%.

**Constitution and Synthesis of Camphor.**—The formula for camphor proposed by Bredt in 1893,

$$
\begin{array}{ccc}
\text{CH}_2\!\!-\!\!-\!\!-\text{CH}\cdots\!\!-\!\!\text{CH}_2 & \leftarrow\!\alpha \\
| \qquad\quad | \qquad\quad | \\
\qquad\quad \text{C(CH}_3)_2\!\leftarrow\!\!-\!\!-\!\!-\!\!\pi \\
| \qquad\quad | \\
\beta\!\rightarrow\text{CH}_2\!-\!-\!-\text{C}\!-\!\!-\!\!-\!\!\text{CO} \\
| \\
\text{CH}_3
\end{array}
$$
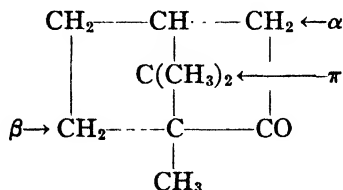
has been verified by Kommpa's synthesis (*Ber.*, 1901, **34**, 2472; 1903, **36**, 4332). It is therefore unnecessary to recite the evidence previously adduced in favour of this and other formulæ. The majority of the chemical reactions of camphor involve only the —$CH_2CO$—group shown on the right-hand side of the formula, and the abbreviated formula $C_8H_{14}\!\!\stackrel{\displaystyle CH_2}{\diagdown}\!\!\stackrel{\displaystyle |}{CO}$ is therefore frequently used to represent the ketone and its simpler derivatives.

Three types of substitution-derivatives are known in addition to those involving the carbonyl group, viz.:

1. *α-Derivatives*, in which the hydrogen of the —$CH_2CO$—group is displaced. Owing to the lack of symmetry in the molecule, the 2 hydrogen atoms do not occupy equivalent positions, and 2 series of stereoisomeric compounds may be prepared. These are frequently distinguished as α-and α′-derivatives, the α-position being that occupied by the halogen, and the α′-position that occupied by hydrogen in the common or α-bromocamphor.

2. *β-Derivatives*, in which a hydrogen atom is displaced from the methylene group which occupies a position in the molecule symmetrically situated with reference to the carbonyl group. These may be prepared by sulphonation (Reychler, Armstrong, and Lowry), by bromination in presence of hydrobromic acid, and indirectly through camphoroxime and hydroxy-camphene (Foerster).

3. *π-Derivatives*, in which a hydrogen atom is displaced from one of the central methyl groups. Substitution in this position can only be effected by sulphonation (Kipping and Pope).

**Oxidation of Camphor.**—The action of oxidising agents on camphor has been the subject of much research, and the products have great theoretical interest. By prolonged treatment with nitric acid of 1.37 sp. gr., camphor is chiefly converted into *camphoric acid*, $C_{10}H_{16}O_4$ (Kosegarten, 1785) which on further boiling is converted into *camphoronic acid*, $C_9H_{14}O_6$; iso-*camphoronic acid*, $C_9H_{14}O_6$, is also formed in small quantities as a by-product of the oxidation of camphor by nitric acid. The oxidation to camphoric acid is a simple change which does not involve the degradation of the molecule, and may be represented by the scheme

$$C_8H_{14}\!\!<\!\!\begin{array}{l}CH_2\\ |\\CO\end{array}\!\!\rightarrow C_8H_{14}\!\!<\!\!\begin{array}{l}CO.OH\\ \\ CO.OH\end{array}$$
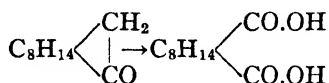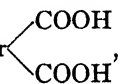
The reverse change from camphoric acid back to camphor has been effected by Haller (*Compt. rend.*, 1896, **122,** 446) and forms the last stage in the synthesis of camphor from its elements by Kommpa's method. The oxidation to camphoronic and isocamphoronic acids is more complex, but both acids have been synthesised, the course of the oxidation is therefore quite clear, and it will be unnecessary to refer to the latter stages in the breaking down of the molecule whereby the constitution of these acids was first established.

$$
\begin{array}{ll}
\begin{array}{l}
CH_2 - CH - CH_2\\
\quad|\qquad|\qquad|\\
\quad|\quad C(CH_3)_2\ |\\
\quad|\qquad|\qquad|\\
COOH\ \ COOH\ COOH\\
\quad\text{Isocamphoronic acid}
\end{array}
&
\leftarrow
\begin{array}{l}
CH_2\!\!-\!\!CH - CH_2\\
\quad|\qquad|\qquad|\\
\quad|\quad C(CH_3)_2\ |\\
\quad|\qquad|\qquad|\\
CH_2\!\!-\!\!C(CH_3)\!\!-\!\!CO\\
\qquad\quad\text{Camphor}
\end{array}
\rightarrow
\\[2em]
\begin{array}{l}
CH_2\!\!-\!\!CH\!\!-\!\!COOH\\
\quad|\qquad|\\
\quad|\quad C(CH_3)_2\\
\quad|\qquad|\\
CH_2\!\!-\!\!C(CH_3)\!\!-\!\!COOH\\
\qquad\text{Camphoric acid}
\end{array}
&
\rightarrow
\begin{array}{l}
COOH\quad COOH\\
\quad|\qquad\quad|\\
\quad|\quad C(CH_3)_2\\
\quad|\qquad\quad|\\
CH_2\!\!-\!\!-\!\!C(CH_3)\!\!-\!\!COOH\\
\qquad\text{Camphoronic acid}
\end{array}
\end{array}
$$
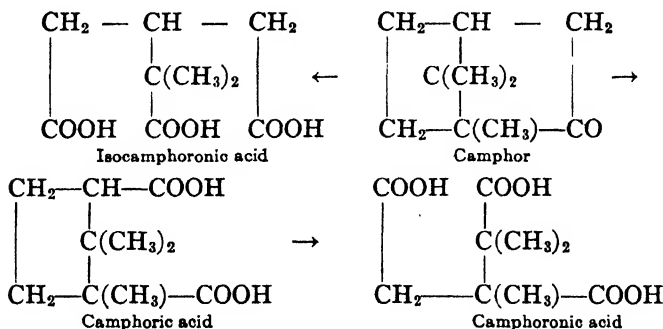
It is noteworthy that in accordance with the above formulæ isocamphoronic acid, unlike camphoronic acid, can only be produced by direct oxidation of camphor, and is not formed in the further oxidation of camphoric acid. Camphoric and camphoronic acids are also formed on oxidising $\alpha$-bromocamphor, $C_8H_{14}\!\!<\!\!\begin{array}{l}CHBr\\ |\\CO\end{array}$ , with

nitric acid; under similar conditions $\beta$-bromocamphor, $C_8H_{10}Br\begin{array}{c}CH_2\\ |\\ CO\end{array}$,

gives $\beta$-bromocamphoric acid, $C_8H_{10}Br\begin{array}{c}COOH\\ COOH\end{array}$, while in presence

of silver nitrate *iso*-camphoronic acid is the main product; these reactions are likewise in accord with the above formulæ, and are seen to represent the normal course of oxidation in substances so constituted. Camphoric acid appears again as the chief product of the oxidation of camphor by potassium permanganate in the presence of caustic alkali; neutral permanganate has but little action on camphor. Dilute chromic acid mixture acts with difficulty on camphor, but by prolonged treatment camphoronic and *iso*-camphoronic acids are produced.

**Camphoric acid,** $C_8H_{14}(CO.OH)_2$, separates from alcohol in monoclinic crystals which melt at 186°, and at a somewhat higher temperature lose water and are converted into the anhydride. Camphoric acid dissolves in 160 parts of cold water or in 10 parts at the b. p., and is readily soluble in alcohol, ether, and fixed oils. From acetone it crystallises with half a molecular proportion of acetone of crystallisation (Pope). It is employed in medicine for the treatment of urinary calculi and vesical catarrh. A 1% solution has been recommended in acute and chronic affections of the respiratory passages. Camphoric acid, as ordinarily prepared, is dextrorotatory ($[a]_D = +46°$), but a lævorotatory modification can be obtained by the oxidation of lævo-camphor. The two varieties combine to form an inactive racemic camphoric acid which melts at 204°, and is less soluble than its isomerides. Inactive camphoric acid may also be obtained by oxidising inactive camphor at 100° by nitric acid.

Camphoric anhydride, $C_8H_{14}(CO)_2O$, prepared by heating the acid alone or with acetic anhydride, crystallises from alcohol in magnificent needle-shaped crystals, m. p. 217°; the preparation of the anhydride affords an excellent method of characterising the acid. The *alkali* salts are freely soluble in water; the *calcium* salt, $CaC_{10}H_{14}O_4$ is moderately soluble; the salts of the heavy metals are insoluble in water. The *esters* prepared by condensing the anhydride with alcohols are oily liquids. The acid *phenyl ethers*, prepared by the action of their sodium derivatives on camphoric anhydride

(Schryver, *Trans.*, 1899, **75,** 663) are of interest as possible therapeutic agents:

*Phenyl hydrogen camphorate,* $C_6H_5O.CO.C_8H_{14}.CO.OH$, m. p......... 100°
*Thymyl hydrogen camphorate,* m. p.............................. 89°
*Guiacyl hydrogen camphorate,* m. p.............................. 112°
*Diguiacyl-camphorate,* m. p...................................... 124°
*Eugenyl hydrogen camphorate,* m. p................... ............ 115.5°
*Naphthyl hydrogen camphorate,* m. p........................... 121–122°

Camphor does not form a compound with sodium hydrogen sulphite, this behaviour being, as a rule, limited to aldehydes and methyl-ketones, though some other ketones show the same reaction. The *phenyl-hydrazone,* $C_{10}H_{16}:N.NHC_6H_5$, is an oil, and is therefore useless for separating or identifying the ketone. The *oxime,* $C_{10}H_{16}:NOH$, is, however, a crystalline compound, and may be used for the detection of camphor. It is formed when a solution of camphor in alcohol is treated with a concentrated aqueous solution of hydroxylamine hydrochloride, sodium carbonate added till the liquid is alkaline to litmus, and the solution diluted with alcohol and allowed to stand for 8 days. The liquid is then largely diluted with water, when the camphoroxime is precipitated; or the alcohol may be removed by evaporation and the residue extracted with ether. On evaporation of its ethereal solution camphoroxime crystallises in white needles, but from alcohol it separates in transparent prisms, which have an odour like camphor and gyrate on water. Camphoroxime melts at 118°, and boils with slight decomposition at 249°. It is nearly soluble in water, but dissolves in alcohol, ether, solutions of alkali hydroxides, and acids.

The *semicarbazone,* $C_{10}H_{16}:N.NH.CO.NH_2$, is also a crystalline compound, m. p. 236–238°.,

Like the open-chain ketones described at the beginning of the section camphor possesses the property of forming an *enolic benzoyl-derivative,*

$$C_8H_{14}\!\!\begin{array}{l}\diagup CH\\ \ \ ||\\ \diagdown C.O.CO.C_6H_5,\end{array}$$
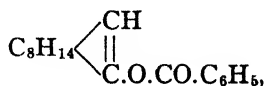
when boiled with benzoyl chloride (Lees, *J. Chem. Soc.,* 1903, **83,** 152); this is an oil boiling at 215 to 220° under 50 mm. pressure, and is slightly lævorotatory, giving $\alpha_D$ $-1°$ $5'$ in a 25 mm. tube; when boiled with alcoholic potassium hydroxide it is converted into camphor and potassium benzoate; with hydroxylamine it gives

camphoroxime and benzoic acid; with bromine it gives $\alpha$-bromo-camphor and benzoyl bromide.

*Sodium-camphor*, prepared by the action of sodium or, better, of sodamide, on camphor dissolved in ether or benzene, is probably the enolic compound $C_8H_{14} \diagdown \begin{array}{l} CH \\ || \\ C.ONa \end{array}$ .
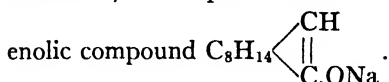
It is immediately decomposed by water, but is of importance in many synthetical operations; when acted on by carbon dioxide it gives the sodium salt of *camphor-carboxylic acid*, $C_8H_{14} \diagdown \begin{array}{l} CH.CO_2H \\ | \\ CO \end{array}$ ;
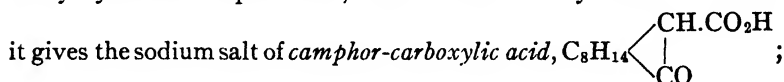
with amyl formate it gives *formyl* or *oxymethylene camphor*,
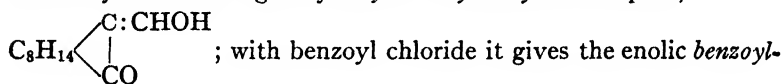
$C_8H_{14} \diagdown \begin{array}{l} C:CHOH \\ | \\ CO \end{array}$ ; with benzoyl chloride it gives the enolic *benzoyl-derivative of $\alpha$-benzoyl camphor*,

$C_8H_{14} \diagdown \begin{array}{l} C.CO.C_6H_5 \\ || \\ C.O.CO.C_6H_5 \end{array}$ ; with amyl nitrite it interacts to form *iso-nitrosocamphor*, $C_8H_{14} \diagdown \begin{array}{l} C:NOH \\ | \\ CO \end{array}$ , from which *camphorquinone*,

$C_8H_{14} \diagdown \begin{array}{l} C=O \\ C=O \end{array}$ , may readily be prepared.
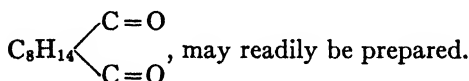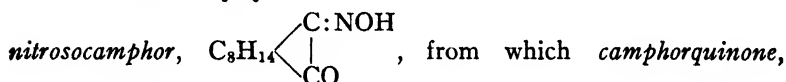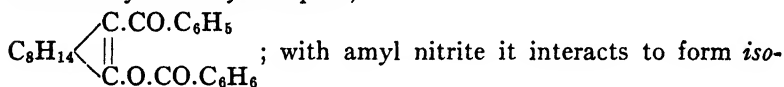
Like other ketones, camphor may be reduced to a secondary alcohol, the product being in this case a mixture of the 2 stereo-isomeric borneols represented by the formula

$$C_8H_{14} \diagdown \begin{array}{l} CH_2 \\ | \\ CH.OH. \end{array}$$
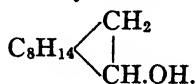
The reduction does not take place readily, but may be effected by the action of sodium and alcohol.

$\alpha$-**derivatives of Camphor.**—$\alpha$-*bromocamphor*, $C_8H_{14} \diagdown \begin{array}{l} CHBr \\ | \\ CO \end{array}$ ,
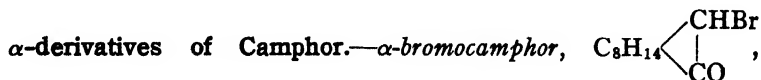
is prepared by heating camphor on a water-bath, and slowly running in slightly more than 1 molecular proportion of bromine, the hydro-gen bromide which is liberated being condensed with water in a

coke-tower. After driving off as much as possible of the hydrogen bromide, the hot and oily material is shaken with a little aqueous potassium hydroxide, poured into a large quantity of water, and recrystallised from alcohol. It separates in long needles, and when pure has m. p. 76° and b. p. 274°. It may be distilled without much decomposition, but the distillation is best carried out under reduced pressure or by means of a current of steam. Bromocamphor is nearly insoluble in water, sparingly soluble in glycerin, moderately (1:8) in olive oil and 90% alcohol (1:12), and readily soluble in ether, chloroform, and benzene.

It is strongly dextrorotatory, giving $[\alpha]_D + 139°$ in saturated alcoholic solution.

When boiled with a solution of silver nitrate, it is decomposed, a precipitate of silver bromide being formed. Bromocamphor is soluble without decomposition in cold concentrated sulphuric acid, and is precipitated unaltered when the solution is poured into excess of water. When treated in alcoholic solution with potassium hydroxide or sodium amalgam, bromocamphor is reduced to camphor. When treated with sodium in toluene solution, it yields sodium-camphor Bromocamphor is employed in medicine as a sedative and hypnotic, and has been found specially useful in cases of hysteria, dipsomania, and delirium tremens.

$$\alpha\alpha'\text{-}dibromocamphor,\ C_8H_{14}\Big\langle\begin{matrix}CBr_2\\|\\CO\end{matrix},$$

prepared by acting on camphor with 2 molecular proportions of bromine, crystallises from alcohol, m. p. 61,° and gives $[\alpha]_D + 40°$ in nearly all solvents; it is very readily reduced to $\alpha$-bromocamphor by alcoholic sodium or potassium hydroxide.

$$\alpha\alpha'\text{-}bromonitrocamphor,\ C_8H_{14}\Big\langle\begin{matrix}CBr.NO_2\\|\\CO\end{matrix},$$

prepared by the action of nitric acid on $\alpha$-bromocamphor (about half the bromocamphor is oxidised to camphoric acid, and half nitrated), has m. p. 107°, and gives $[\alpha]_D - 22.0°$ when dissolved in chloroform, $[\alpha]_D - 54°$ in benzene.

$$\alpha'\text{nitro-camphor},\ C_8H_{14}\Big\langle\begin{matrix}CH.NO_2\\|\\CO\end{matrix},\quad \text{prepared by reducing}$$
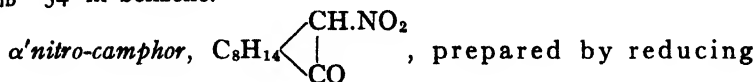
$\alpha\alpha'$-bromonitrocamphor in alcoholic solution with sodium ethoxide (camphor cannot be nitrated directly), m. p. 102°. Although itself lævorotatory, it forms a series of strongly dextrorotatory *salts*, and a dextrorotatory *anhydride*, m. p. 196°, derived from a hydroxylic

isomeride, $C_8H_{14}\begin{cases} C:NO_2H \\ | \\ CO \end{cases}$ . A partial conversion of the normal

compound into the acidic isomeride takes place in solution and is accompanied by a change of rotatory power from left toward right, *e. g.*, in benzene from −124° to −104°.

$$\alpha\text{-}chlorocamphor,\ C_8H_{14}\begin{cases} CHCl \\ | \\ CO \end{cases},$$
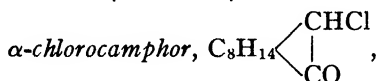
prepared by the action of chlorine on camphor dissolved in alcohol, crystallises from alcohol in long glistening needles, m. p. 93°, and gives $[\alpha]_D + 96°$ in alcohol.

$$\alpha\alpha\text{-}dicamphorarsinic\ acid,\ C_8H_{14}\begin{cases} \overset{\displaystyle O}{\overset{\|}{CH-As-CH}} \\ |\quad\ O\quad | \\ CO\ \ H\ \ CO \end{cases}C_8H_{14},$$
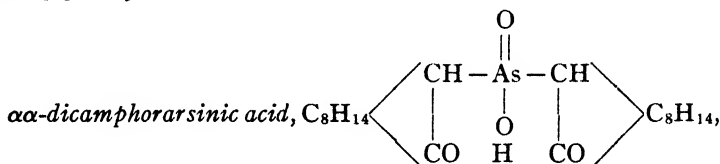
Prepared by the action of arsenious chloride on sodium camphor, it is almost insoluble in water, but separates from alcohol in lustrous prisms, m. p. with decomposition 266°; $[\alpha]_D + 186.6°$ in chloroform. The *alkali* salts dissolve readily in water; the *silver* and *cadmium* salts are sparingly soluble crystalline precipitates (Morgan and Mickelthwaite, *Trans.*, 1908, **93**, 2144–2148).

### β-derivatives of Camphor

*Camphor β-sulphonic acid*, $C_{10}H_{15}O.SO_2OH$, separates in a crystalline form when a mixture of camphor (1 mol.) acetic anhydride (2 mols.), and sulphuric acid (1 mol.) is allowed to stand for 2 or 3 days (Reychler); it is readily soluble in water, from which it separates with $1H_2O$, crystallises well from acetic acid or ethyl acetate, m. p. 193°, and gives $[\alpha]_D + 21°$ in water. The *amide*, $C_{10}H_{15}.SO_2.NH_2$, has m. p. 132°, and the *anhydramide*, $C_{10}H_{15}SO_2N$, formed by removal of a molecule of water from the amide, melts at 223°. The *sulphochloride*, $C_{10}H_{15}SO_2Cl$, has m. p. 68°; the *sulphobromide*,

$C_{10}H_{15}O.SO_2Br$, melts at 93°, and when heated in boiling xylene loses sulphur dioxide and gives β-bromocamphor.

*β-bromocamphor*, m. p. 78°, gives $[α]_D + 19°$ only; it can be distinguished from the α-isomeride most readily by determining the m. p. of a mixture with the α-compound; this mixture melts at a much lower temperature than either of the isomerides separately.

*αβ-dibromocamphor*, $C_8H_{13}Br\begin{matrix} CH.Br \\ | \\ CO \end{matrix}$, prepared by brominating camphor in a sealed tube (when the HBr converts the αα' into the αβ compound), by brominating the preceding compound, or by decomposing α-bromocamphor β-sulphobromide, has m. p. 113°.

*β-chlorocamphor*, prepared by Foerster's method, melts at 132.5°. *α-chloro β-bromocamphor*, prepared in much the same way as the dibromocompound, has m. p. 98°.

*Camphor β-thiol*, prepared by reducing the β-sulphochloride with tin and hydrochloric acid, melts at 66°, gives $[α]_D + 6°$ in acetone.

## π-derivatives of Camphor

*Camphor π-sulphonic acid*, $C_{10}H_{15}O.SO_2.OH$, prepared by the action of chlorosulphonic acid on camphor, is most readily separated in the form of the *ammonium* salt. The *amide*, $C_{10}H_{15}O.SO_2.NH_2$, has m. p. 135–137.5°, and forms an *acetyl*-derivative, m. p. 199°. The *sulphochloride*, $C_{10}H_{15}O.SO_2Cl$, melts at 137.5°, losing a molecule of sulphur dioxide and giving *π-chlorocamphor*, $C_{10}H_{15}ClO$, m. p. 139°. The *sulphobromide*, $C_{10}H_{15}O.SO_2Br$, melts in a similar manner at 145° with formation of $SO_2$ and *π-bromocamphor*, $C_{10}H_{15}BrO$, m. p. 93°.

α-Chlorocamphor gives a *sulphonamide* m. p. 150°, a *sulphochloride* m. p. 124°, and a *sulphobromide* m. p. 145°, the products arising from the fusion of the latter compounds being $SO_2$ and *απ-dichlorocamphor* m. p. 118°, or *απ-chlorobromocamphor*, m. p. 138°.

*α-bromocamphor π-sulphonic acid* has been extensively used for resolving racemic bases into their optically active constituents. The *sulphonamide*, has m. p. 145°; the *sulphochloride*, m. p. 136–137°, and the *sulphobromide*, melts at 145°, giving $SO_2$ and *απ-bromochlorocamphor*, m. p. 133°, or *απ-dibromocamphor*, m. p. 152–153°.

## Menthone, $C_{10}H_{18}O$

Menthone is the ketone corresponding with the alcohol menthol, with which it occurs in oil of peppermint. It exists in both the *dextro-* and the *lævo-*rotatory forms, and as it is probable that no natural specimen has been isolated which did not consist of mixtures of the optical antipodes, the optical rotation cannot be stated with precision. The characters of natural menthone, however, fall within the following limits:

Sp. gr. at 15.5°.............................. 0.894 to 0.899
Opt. rot. ...................................... up to ±35°
Ref. index at 20° ............................ about 1.4495
B. p. ......................................... 207°–208°

Four isomeric methones are possible, owing to the complicated stereochemical relationships.

The constitution of menthone is

$$CH(CH_3)$$

$$H_2C \diagup \diagdown CH_2$$

$$H_2C \diagdown \diagup CO$$

$$CH.CH(CH_3)_2$$
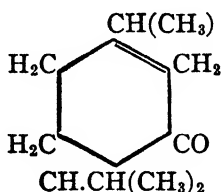
Menthone has been produced synthetically by Kötz and Hesse (*Ann.* 1905, **342**, 306) by condensing methyl-hexanone with ethyl oxalate. It is also produced by the reduction of piperitone by Smith and Penfold (*J. Proc. Roy. Soc. N. S. W. Liv.* **45**) who give the following as the characters of the resulting menthone (the slight optical activity being, no doubt, due to traces of impurities).

Sp. gr. at 15.5°.............................. 0.8978 at 20°
B. p............................................ 208°
Ref. index at 20° ............................ 1.4529
Opt. rot. ..................................... −0°.15
M. p. of oxime................................ 80°

## Fenchone, $C_{10}H_{16}O$

This ketone was discovered by Wallach in 1890, and is an important constituent of fennel oil (from *Fœniculum vulgare*), whilst a lævorotatory form occurs with the isomeric ketone thujone in Thuja oil. Its characters are as follows:

B. p. ........................................... 192°–198°
M. p. ........................................... +5° to +6°
Sp. gr. at 15.5°................................. 0.950
Ref. index at 20° ............................... 1.4630
Sp. rot.......................................... about +70°

It differs from camphor in being very resistant both to nitric acid and to bromine, does not react with phenylhydrazine or sodium hydrogen sulphite, does not form an oxymethylene derivative and cannot be sulphonated by Reychler's method. Phosphoric oxide converts it into *m*-cymene, where camphor gives *p*-cymene, and the formula

$$CH_2{-}CH{-}CH{-}CH_3$$
$$\qquad\quad \mid$$
$$\qquad C(CH_3)_2$$
$$\qquad\quad \mid$$
$$CH_2{-}CH{-}CO$$
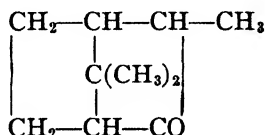
has therefore been proposed by Wallach (*Annalen*, 1898, **300**, 319). As, however, its behaviour is entirely different from that of *α*-methyl-camphor, this formula can scarcely be upheld, and the following formula, due to Aschan (*Annalen*, **387**, 1) is now generally accepted

$$(CH_3)_2C{-}{-}{-}CH{-}{-}{-}CH_2$$
$$\qquad\mid \qquad\quad CH_2 \qquad\quad \mid$$
$$\qquad\mid \qquad\quad \mid \qquad\quad \mid$$
$$\quad CO{-}{-}{-}C(CH_3){-}CH_2$$
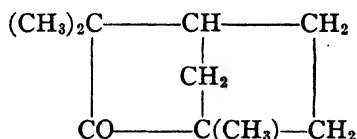
Fenchone shows the normal properties of a ketone: the *oxime* prepared from natural fenchone melts at 165°. That prepared from optically inactive fenchone melts at 158°–160°. The semicarbazone (active) melts at 182°–183°, and (inactive) at 172°–173°. The secondary alcohol *fenchyl alcohol*, $C_{10}H_{17}OH$, prepared by the action of sodium and alcohol, melts at 45°, boils at 201°, and has a specific rotatory power $[\alpha]_D \pm 10.6°$, the alcohol being opposite in sign to the ketone.

### Pulegone, $C_{10}H_{16}O$

Pulegone is the chief constituent of oil of pennyroyal (from *Mentha pulegium*). Unlike the preceding compound, it forms a *bisulphite-compound*, which may be utilised in the isolation of the ketone. Its characters are as follows:

B. p. .............................................. $221°$–$222°$
Sp. gr. at $15.5°$ ................................... 0.940
Sp. rot. ........................................... $+22.9°$
Ref. index at $20°$ ................................. 1.4880

Its constitution has been established by synthesis (Tiemann and Schmidt, *Ber.*, 1896, **29**, 913).

$$CH_3.CH\diagup\begin{matrix}CH_2-CO\\ CH_2-CH_2\end{matrix}\diagdown C = C\diagup\begin{matrix}CH_3\\ CH_3\end{matrix}$$
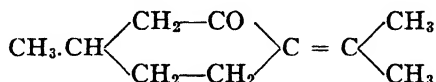
In accordance with this formula, it is converted by reduction into menthone and menthol, and by oxidation into $\beta$-methyladipic acid,

$$CH_3.CH\diagup\begin{matrix}CH_2-COOH\\ CH_2-CH_2\end{matrix}\diagup CO.OH$$
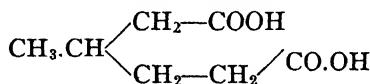
The *oxime* melts at $123°$–$124°$, but owing to molecular rearrangement, it appears to be the oxime of *iso*pulegone. The *semicarbazone* melts at $172°$.

For the detection of pulegone, equal volumes of the ketone and petroleum-spirit are mixed with a little amyl-nitrite, the mixture cooled thoroughly, and a drop of hydrochloric acid added. If pulegone be present, white nitrosopulegone separates and the liquid becomes blue in colour. 1% of pulegone may thus be detected.

## Thujone, $C_{10}H_{16}O$

Thujone is a ketone present in the oils of thuja, tansy, and wormwood, and is identical with the substances previously described as tanacetone and salvone. It may be prepared conveniently by treating 200 grm. of wormwood oil with 200 c.c. of a saturated solution of sodium hydrogen sulphite, 75 c.c. of water, and 300 c.c. of alcohol. The mixture is shaken at intervals for a fortnight, when the crystals of the addition compound which separate are washed with ether-alcohol, and the thujone set free by sodium hydroxide solution.

Thujone consists of two if not three physical isomerides and natural thujone always consists of a mixture of the two well characterised substances $\alpha$-thujone and $\beta$-thujone.

Wallach has shown that thuja oil contains essentially $\alpha$-thujone and oil of tansy $\beta$-thujone. Wormwood oil contains a mixture in which $\beta$-thujone predominates. Fractional crystallisation of the

semicarbazones forms a method of separating and purifying the isomers. Pure $\alpha$-thujone has the following characters:

B. p. ................................................ 200°–201°
Sp. gr. at 15.5°.................................... 0.9125
Ref. index at 20° ................................. 1.4510
Sp. rot. .......................................... −10.23′

$\beta$-thujone is dextrorotatory, but does not appear to be the optical antipode of $\alpha$-thujone. Its sp. rot. is +76°, and its oxime melts at 54–55°.

According to Wallach the characters of natural thujone (*i. e.* a mixture of $\alpha$-thujone and $\beta$-thujone) are approximately

B. p. ................................................ 200°–201°
Sp. gr. at 15 5°.................................... 0.912
Ref. index at 20°.................................. 1.4503

Thujone has the following constitution:

$$C.CH(CH_3)_2$$

H₂C ... CH₂

HC ... CO

CH.CH₃
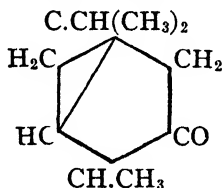
Thujone forms a tribromo-derivative, $C_{10}H_{13}Br_3O$, m. p. 121°, an oxine, m. p. 55°, and a carbazone, m. p. 171°. By treatment in alcoholic solution with sodium, it is almost entirely converted into *thujyl alcohol*, $C_{10}H_{17}OH$, an isomer of linalol occuring in oil of tansy.

Prolonged heating with strong sulphuric acid coverts thujone into *isothujone;* and when heated alone to 280°, thujone is coverted into another isomer called *carvotanacetone*.

## Carvone, $C_{10}H_{14}O$

A doubly-unsaturated cyclic ketone, formerly known as carvone, occurs both in the dextrorotatory and in the lævorotatory form, in the essential oils of dill, caraway and kuromoji. *d*-Carvone occurs to the extent of 50% or more in oil of caraway, together with nearly as much limonene. It is also present to the extent of 30% in the oils of dill and fennel, while *l*-carvone occurs in the oils of *Mentha crispa* and kuromoji.

Pure dextro-carvone may be prepared by treating the fraction of caraway oil distilling above 190° with an equal volume of alcoholic ammonium sulphide, when a substance of the composition $C_{10}H_{14}(OH).(SH)$ separates in long needles, which on treatment with alcoholic potassium hydroxide are decomposed with separation of carvone.

Carvone is official in the German Pharmacopœia (carvol), in which it is described as a pale yellowish or colourless liquid, having a strong odour of caraway.   Carvone has the following characters:
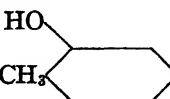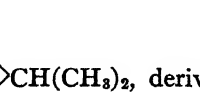
Sp. gr. at 15.5°.................................... 0.964
Opt. rot............................................ ±59° 30′
Ref. index at 20° ................................. 1.5020
B. p. .............................................. 224°

1 c.c. of carvone diluted with an equal measure of alcohol is stated to remain unchanged or to assume only a slight or violet colour on addition of a drop of a very dilute solution of ferric chloride.   Pure carvone has the practical advantage of being much more readily soluble in dilute alcohol than is the case with oil of caraway, while it possesses all the valuable properties of the natural oil.

Carvone shows all the characteristic reactions of a ketone.   The *oxime* (from the active varieties), $C_{10}H_{14}:NOH$, m. p. 72°, is identical with nitrosolimonene, indicating a close relationship between the two parent substances.   The oxime of the optically inactive variety melts at 93°; it forms a *benzoyl* derivative, m. p. 95°.   The *semicarbazone* melts at 162 to 163° (active) or 154–155° (inactive).

When boiled with excess of sodium hydrogen sulphite, the ketone is converted into a substance which, according to Labbé, has the formula $C_{10}H_{14}O(SO_3NaH)_2$.

On treating it with metaphosphoric acid, great heat is evolved and actual explosion is apt to occur.   With crude caraway oil the action is less intense.   In either case, the ketonic substance carvone is converted into the isomeric substance *carvacrol*, a phenol of the formula $CH_3$—(HO)—$CH(CH_3)_2$, derived from the hydrocarbon *p*-cymene and differing from thymol only in the orientation of the hydroxyl group.

Carvacrol occurs in several essential oils, especially those of the thyme family.   It is the principal constituent (50 to 80%) of Spanish

oil of hops, of Cretan oil of marjoram (from *Origanum hirsutum* and *creticum*), and also occurs in the oils of caraway and pepper-wort (*Satureja hortensis*). In smaller quantity, carvacrol exists, together with thymol and cymene, in the oil from *Thymus serpyllum*.

The carvacrol occurring naturally in essential oils is probably a product of the molecular transformation of previously existing carvone, the—CH.CO—group being rearranged to form the C:C(OH)—group. The same change can be effected by heating carvone with alcoholic potassium hydroxide.

## Estimation of Carvone

The estimation of this important constituent of certain essential oils (*e. g.*, the oils of caraway, cumin, dill, spearmint, etc.) cannot be made with any degree of accuracy. Several methods have been proposed, as, for example, those based on a estimation of the iodine absorption of the oil, and on the results obtained by fractional distillation. Neither of these processes, however, gives more than an indication of the carvone content. The specific gravity and the optical rotation of the carvone-containing oils are, of course, valuable data, but give only a rough approximation to the percentage of carvone.[1]

A promising method for the estimation of carvone, based on the formation of a crystalline carvoxime, has been proposed and studied by E. Kremers (*J. Soc. Chem. Ind.*, 1901, **20**, 16) and his collaborators (*Pharm. Rev.*, 1896, 76; *Pharm. Arch.*, 1899, **2**, 81–91; 1900, **3**, 9–18). (See also Alden and Ehlert, *Chem. Centr.*, 1897, ii, 146.) A known weight of the oil under examination, containing about 5 grm. of carvone, is dissolved in 25 c.c. of alcohol, and 5 grm. of hydroxylamine hydrochloride and 6.5 grm. of sodium hydrogen carbonate

[1] Assuming that caraway oil contains only limonene and carvone, and that *a* represents the sp. gr. of the sample, the percentage of carvone (*x*) may be deduced from the following formula:

$$x = \frac{(a - 0.850)100}{0.112}$$

0.850 is the sp. gr. of limonene, and 0.112 the difference between this and the sp. gr. of carvone (0.962).

A process in which the crystalline hydrogen sulphide addition product is isolated and the carvone regenerated and weighed, is rendered useless as a quantitative method by the fact that the carvone hydrosulphide remains partly in solution, and also other constituents in the oils are apparently acted on by hydrogen sulphide.

Another method which has been largely employed for the estimation of carvone is that in which the crystalline carvone-phenyl-hydrazone, resulting from the reaction of the carvone with phenyl-hydrazine at 100°, is isolated and weighed after purification. The compound, however, is unstable and cannot be dried without decomposition, and the method thus gives only approximate results.

are added.[1]   The mixture is boiled for 15 to 20 minutes on the
water-bath under a reflux condenser; 25 c.c. of water are next intro-
duced, and the alcohol is distilled off, a large quantity of limonene
simultaneously passing over.   Steam is then passed slowly through
the flask and the distillation continued, collecting the last portions
of the distillate in separate test-tubes, till traces of carvoxime crys-
tals appear on the surface of the liquid.[2]   The distillation is stopped,
the condenser rinsed with a little hot water, which, together with
the last distillates, is returned to the flask.   The whole is cooled,
and when the oxime has solidified it is collected on a filter (removing
what adheres to the flask by means of a loop of stiff wire), washed,
and dried by suction.   The air-dried product is finally heated for
1 hour on the water-bath and weighed.   To the weight thus obtained
0.100 grm. is added to compensate for the loss by volatilisation and
the carvoxime so corrected is calculated into carvone by the factor
0.9088.[3]   The method gives results which are fairly uniform, but
are usually about 2% too low.   It is necessary that the directions
should be strictly followed to obtain satisfactory results.   Kremers
considers the method by no means perfect, but of much value, and
it has the advantage of yielding a definite crystalline compound.

When an oil is badly resinified, the carvoxime may refuse to crys-
tallise, and in such case the oil should be distilled with steam, and
the process carried out on the distillate.   A small quantity of resin
will increase the weight of oxime recovered, and so tend to make the
results too high.   The m. p. of the carvoxime, which should lie
between 71° and 73°, is lowered by the presence of resin, but no
idea of the amount of impurity can be obtained in this way, as the
point at which melting begins in the impure oxime is not sharp.

J. Walther (*J. Pharm. Chim.*, 1901, **13**, p. 32) has proposed to
estimate carvone by titrating the excess of hydroxylamine hydro-
chloride remaining after the removal of the carvoxime.

Bennett and Donovan (*Analyst* 1922, **47**, 146) have critically
examined   the   hydroxylamine   process   (*vide under Citral*) as a

---

[1] It is desirable not to use more sodium hydrogen carbonate than is necessary to liberate
the whole of the hydroxylamine.   Kremers' experiments, indeed, show that the amount of
sodium bicarbonate may be advantageously reduced to 5.5 grm. instead of employing 6.5
grm. as recommended in the text.   A large excess of hydroxylamine hydrochloride should
be avoided.   If more than 50 % of carvone is supposed to be present, the amount of hydroxyl-
amine is correspondingly increased.
[2] If the distillation of the carvoxime and alcohol mixture is not carried out carefully in
the manner described, loss may be entailed by carrying the distillation too far.   Schimmel
& Co. failed to obtain satisfactory results by this method (Semi-Annual Report, October,
1896, p. 49), probably for this reason.
[3] The volatility of carvoxime in presence of water-vapour is somewhat irregular, and the
drying of the compound should always be conducted under similar conditions.

method for the estimation of carvone. They suggest that the hydroxylamine hydrochloride of commerce frequently contains impurities which render the end point of the titration (to phenolphthalein) very obscure, and consider it advisable to recrystallise the reagent from hot water. They carried out a series of experiments with specially purified carvone with the following results:

|  | CARVONE TAKEN | CARVONE FOUND % OF THAT TAKEN | TIME OF BOILING |
|---|---|---|---|
| 1 | 1.101 | 99.1 | 20 minutes |
| 2 | 1.006 | 99.9 | 30 minutes |
| 3 | 0.534 | 105.3 | 30 minutes |
| 4 | 1.000 | 93.4 | 10 minutes |
| 5 | 1.000 | 91.1 | 10 minutes |
| 6 | 0.500 | 100.4 | 12 minutes |
| 7 | 0.500 | 99.8 | 10 minutes |
| 8 | 0.500 | 105.0 | 2 hours |
| 9 | 1.005 | 99.6 | 20 minutes |
| 10 | 0.598 | 100.3 | 20 minutes |
| 11 | 0.499 | 103.7 | 20 minutes |

It is seen therefore that accurate results are obtained by boiling the carvone for not less than 20 minutes with a moderate excess of hydroxylamine solution, that is so that about $\frac{1}{3}$ of the quantity used is in excess.

The conditions of the analysis are of considerable importance. If, for example, the excess of hydroxylamine is much above that indicated, the time of boiling must be reduced, whilst if the excess is below that indicated, the reaction is incomplete even after long boiling.

It is therefore absolutely necessary to observe the above mentioned conditions as to firstly the excess of hydroxylamine solution should be about 30% of the total employed, and secondly the time of boiling should be from 20 to 30 minutes. By standing in the cold for 12 to 18 hours, equally good results are obtained, and varying excess of hydroxylamine solution has no effect on the results. For example, where 0.5 and 1.0 gram of carvone were taken and the same quantity of hydroxylamine solution was used in both cases, the results were identical, namely 99.8%.

It is obvious, therefore, that the hydroxylamine process carried out as described under citral determination, with the above conditions attached, forms an accurate method for the estimation of carvone in essential oils.

For the separation of carvone from limonene, H. Labbé (*Bull. Soc. Chim.*, 1900, **23**, 280) boils together 5 grm. of the oil and 15 of

sodium hydrogen sulphite, with water and some sodium bicarbonate, for 1.5 hours in a small flask fitted with a reflux condenser. The product is shaken out with ether, the separated ethereal layer dried by anhydrous sodium sulphate, and the residual limonene, etc., weighed. The carvone is estimated by difference.

**Eucarvone and isocarvone** are two ketones isomeric with carvone; the former gives an *oxime*, m. p. 106°, and a *semicarbazone*, m. p. 184°; the latter gives an *oxime*, m. p. 98°; neither compound has been detected as a natural product.

## (G) ESTERS

It is now well established that the esters occurring in essential oils are amongst their most important odorous constituents. So much so is this a fact, that it led to the definite valuation of a number of essential oils on their ester contents. This idea was carried to excess and became known as the "ester theory" especially in Germany. Where the ester, or group of esters, forms almost the sole odorous consitutent of an oil, such a valuation is, of course, approximately accurate. For example, no one could object to a Bergamot oil being valued on its ester content, since it owes practically the whole of its odour value to the linalyl esters it contains. But it is an utterly absurd proposition to value lavender oils on their ester content—except in so far as one is judging a series of lavender oils grown in the same district, where the lavender is hybridising with the spike lavender and the ester value is a fair criterion of value between that particular set of oils. To indicate the absurdity of attempting to value lavender oils on the basis of their ester content one may call attention to the fact that English lavender oil—the most highly esteemed of all lavender oils, contains about 10% of esters, whilst the far cheaper French lavender oils contain up to 40% of more or esters. Further there are lavender oils grown on the Italian frontier containing about 25% of esters, of far finer odour than some of the coarse French lavender oils containing 38–40%. The explanation is, of course, that lavender oil contains other substances besides esters to which its odour owes much of its value. The same is true of geranium and other oils.

The estimation of the percentage of esters is, however, of the highest importance, as, coupled with other estimations, it fre-

quently assists one in coming to a decision as to whether an oil is genuine or not. The ridiculous persistence with which the valuation of essential oils on their ester content has been advocated is directly responsible for the manufacture of a series of artificial esters for the purpose of adulterating essential oils.

The main purpose pursued by the manufacturer of such artificial esters, is to provide those whose saponification values are such, that when calculated into the natural ester of the essential oil being examined, they shall apparently show a much higher percentage of ester than the actual weight employed. Thus the addition of 1% of the tribasic glyceryl acetate would show, on the ordinary method of ester calculation considerably more than 1% of linalyl acetate in bergamot oil. This matter will be fully dealt with under the Analysis of Essential Oils.

The number of esters naturally occurring in essential oils is very large, and, as might have been expected, the chemist has taken advantage of the known odours of natural esters, to prepare a number of others, closely allied to the natural substances, which give the perfumer a long series of artificial esters with which to modify or improve his productions. Only the most important of the natural and artificial esters will be dealt with here.

## Methyl Salicylate

Owing to the fact that oil of wintergreen and oil of sweet birch consist to the extent of about 99% of methyl salicylate, the manufacture of this ester on a commercial scale has now assumed considerable proportions. Except for a slight delicacy in odour, the above mentioned essential oils cannot be distinguished from the artificial ester, and the latter has largely superseded the former—often, unfortunately, illegitimately, as much of the expensive natural oil is adulterated with the artificial ester. Methyl salicylate, $C_6H_4(OH)(COOCH_3)$ has the following characters, which are compared with those of ethyl salicylate, an ester sometimes used for the same purposes.

| | METHYL SALICYLATE | ETHYL SALICYLATE |
|---|---|---|
| Sp. gr. at 15.5°..................... | 1.1815 | 1.1375 |
| B. p............................... | 224° | 234° |
| Ref. index at 20°................... | 1.5375 | 1.5239 |

## Methyl Anthranilate

Methyl anthranilate is an important ester occurring in the oils of neroli, ylang-ylang, jasmin and other flower oils.   It is the methyl ester of *ortho*-aminobenzoic acid, having the constitution

$$
\begin{array}{c}
\text{CH} \\
\text{HC} \diagup \diagdown \text{CH} \\
\text{HC} \diagdown \diagup \text{C.NH}_2 \\
\text{C.COO.CH}_3
\end{array}
$$
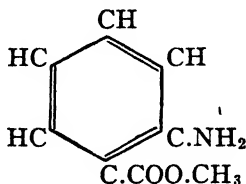
It is prepared artificially by, for example, treating phthalimide with a hypobromite in the presence of alkali, and condensing the resulting anthranilic acid (*o*-aminobenzoic acid) with methyl alcohol.

Methyl anthranilate is a crystalline substance, tending to remain in a state of superfusion.   It has a beautiful blue-violet fluorescence, which is apparent in any essential oil containing it.   Its characters are as follows:

M. p.................................. $24°-25°$
B. p.................................. $132°$ at 14 mm.
Sp. gr. at $15.5°$........................ $1.168$ (at $15°$, superfused).

It yields a red crystalline additive compound with *p*-dimethyl-amido-benzaldehyde, which melts at $181°-182°$, and a picrate melting at $105°-106°$ when alcoholic solutions of the ester and of picric acid are mixed.

Hesse and Zeitschel (*Ber.*, 1901, **34**, 296) give the following method for its quantitative estimation.   About 30 grm. of the oil containing it are dissolved in 2 to 3 times its volume of anhydrous ether.   This mixture is kept at $0°$, and a mixture of 1 part of $H_2SO_4$ in 5 of ether added slowly drop by drop till no further precipitation takes place.   The ester is thus precipitated in the form of a sulphate, as it has strong basic properties.   It is collected, washed with ether, dried and weighed; or it may be titrated with semi-normal alkali. If *p* be the weight of the sample and *n* the number of c.c. of semi-normal potash used, the percentage of methyl anthranilate is

$$\frac{3.775 \times n}{p}$$

Ethyl anthranilate is a closely similar substance, and has a rather sweeter odour than the methyl ester.   It is a liquid boiling at $260°$.

Methyl methyl-anthranilate, $C_6H_4(NH.CH_3)COOCH_3$ is also a very similar compound, and exists in several essential oils. It can be estimated in exactly the same manner as methyl anthranilate. It has the following characters:

M. p. .................................... $18.5°–19.5°$
B. p. .................................... $131°$ at 13 mm.
Sp. gr. at 20° ............................ $1.1238$
Ref. index at 20° ......................... $1.5796$

## Methyl Benzoate

Methyl benzoate $C_6H_5COOCH_3$ exists in various flower oils, and is prepared artificially, being known in commerce as oil of Niobe.

It is essential in the preparation of artificial ylang-ylang oil, and is a favourite ingredient of the perfume known as Peau d'Espagne. It is an oil boiling at 199°, and has a specific gravity 1.1026 and refractive index 1.5770. It should be free from chlorine (*vide* under benzaldehyde) and can be examined by a quantitative saponification, and determination of the melting point of the liberated acid.

## Methyl Cinnamate

Methyl cinnamate, $C_6H_5.CH:CH.COOCH_3$ is found in various balsams. It is made artificially and is used to some extent in the perfume industry. It is a crystalline mass, with a tendency to superfusion, melting at 34°–36°, boiling at 265°, with a specific gravity 1.066 at 40° and refractive index 1.5682 at 35°.

## Amyl Salicylate

Amyl salicylate $C_6H_4(OH)(COOC_5H_{11})$ is a highly odorous ester, forming the basis of all the perfumes of the orchid type. It is known as "orchidée" or "trèfle," in commerce, and when pure has the following characters:

B. p. at 760 mm. ........................ $276°$ to $277°$
Sp. gr. at 15.5° ......................... $1.052$ to $1.054$
Ref. index at 20° ........................ $1.5055$
Opt. rot. ................................ $+2°$

## Geranyl Esters

The esters of geraniol are of such importance to the perfumer that a number of them are now manufactured on a commercial scale. Several of them occur in numerous essential oils, usually associated

with free geraniol, and, according to their nature and quantity, play a very important part in modifying the odour of the main constituent of the oil. In general they may be described as having a rose or geranium odour, which varies according to the acid constituent of the ester. Owing to the expense of separating geraniol in a state of absolute purity, commercial esters of geraniol are seldom quite pure. The following are the principal substances of this series.

*Geranyl formate* $C_{10}H_{17}OOCH$. A good commercial specimen should contain not less than 90% of the ester. The specific gravity should vary between 0.924 and 0.926, it should be optically inactive, and have a refractive index about 1.4650. If necessary, the geraniol can be separated by saponification, when it should correspond approximately in characters with a pure geraniol.

*Geranyl acetate* $C_{10}H_{17}OOC.CH_3$. This ester is employed in perfumery more than any of the others. It is found naturally in many essential oils, and has a sweet rose odour. Its characters are as follows:

Sp. gr. at 15.5°.................................. 0.917
B. p............................................... 242°–245°
Ref. index at 20° ................................. 1.4628 at 15°

Commercial samples should contain at least 95% of the true ester, but a specific gravity between 0.910 and 0.920 is permissible.

*Geranyl butyrate* $C_{10}H_{17}OOC(CH_2)_2CH_3$. This is an ester of very fine, delicate rose odour and is frequently employed to modify and round off the perfume of artificial attar of rose. The isobutyrate is similar in characters, as, to some extent is geranyl isovalerianate.

## Linalyl Esters

Linalyl acetate is the dominating odorous constituent of bergamot oil, and is also a very important constituent of French lavender-oil. This, and other esters of linalol have come into vogue in perfumery exactly as have the corresponding esters of geraniol.

*Linalyl formate,* $C_{10}H_{17}OOCH$ is difficult to manufacture in a pure condition, and commercial samples rarely contain over 85% of the true ester.

*Linalyl acetate* $C_{10}H_{17}OOC.CH_3$. Commercial specimens usually contain about 90 to 95% of the true ester. The specific gravity is about 0.913 at 15.5°, and optical rotation between +6° and −6°.

Its refractive index is about 1.4500. The propionate and butyrate are obtainable but are not used to any great extent.

## Benzyl Esters

Numerous benzyl esters are found in essential oils, but, naturally, would not pay for extraction commercially. The preparation of such esters artificially is not a matter of difficulty and those that are required for perfumery purposes are now manufactured on a commercial scale.

*Benzyl acetate*, $C_6H_5.CH_2.COOCH_3$ is a constituent of various flower oils, such as jasmin, ylang-ylang, etc. It is a colourless oil of specific gravity 1.057 at 15.5°, refractive index 1.5034 at 20°, and boils at 206°. The commercial article is practically pure, and should indicate 99–100% of true benzyl acetate on saponification, the separated acid having the melting point and general characters of benzoic acid.

*Benzyl benzoate*, $C_6H_5.CH_2.COOC_6H_5$ is a constituent of the essential oils of tuberose, and ylang-ylang, and of balsam of Peru. It is prepared artificially on a considerable scale, because it is one of the best solvents of artificial musk, and is also a very valuable fixative in perfumery. Its odour is not very powerful, so that it can be used as a fixative with most floral perfumes, without imparting too marked an odour to the bouquet. Benzyl benzoate is, when absolutely pure a crystalline solid melting at 21°, but as it tends to exist in a state of superfusion, commercial specimens are almost invariably liquid at ordinary temperature. The best samples have characters which fall within the following limits:

Sp. gr. at 15.5°............................ 1.120 — 1.122
B. p. at 760°.............................. 310°–325°
Ref. index at 20° ......................... 1.5670 to 1.5690

**Benzyl cinnamate,** $C_6H_5.CH_2COO.CH:CH.C_6H_5$ is one of the principal odorous constituents of the heavy essential oils distilled from such substances as storax, balsam of Tolu and balsam of Peru. It is a crystalline substance with a sweet, heavy balsamic odour recalling that of the oriental type of perfume. It has the following characters:

M. p. ........................................... 39°
B. p............................................ 335°–340°

Commercial specimens rarely have a melting point over 31°–34.° They contain from 96–98% of true benzyl cinnamate. The acid

liberated on saponification should possess the melting point and general characters of pure cinnamic acid.

## Bornyl Acetate

The esters of borneol possess a fine odour of pine needles, and are manufactured to enable the perfumer to produce artificial pine odours. The principal natural ester, which is responsible for the pine odour is bornyl acetate, $C_{10}H_{17}COO.CH_3$. It is a liquid of delicate and refreshing odour, and as it can be manufactured at a reasonable cost, it is used to a considerable extent in perfumery bath salts, disinfecting theatres, etc., etc. It is a crystalline substance having the following characters:

| | |
|---|---|
| M. p. | 29° |
| Sp. gr. at 15.5° | 0.991 |
| Ref. index at 20° | 1.4660 |
| B. p. at 10 mm. | about 98° |
| Opt. rot. | ±40° |

The artificial substance should contain from 96 to 98% of bornyl acetate as indicated by a saponification, and the separated alcohol should have, approximately, the characters of borneol. Bornyl formate, $C_{10}H_{17}.COO.H$ also occurs naturally, and is also prepared artificially. It is a liquid of specific gravity about 1.017, refractive index 1.4708, and boils at about 225°–230°. Bornyl butyrate, propionate and valerianate are all manufactured on a small scale, and are used to some extent in perfumery. They should all contain over 95% of ester, and should have the following characters:

| | BUTYRATE | PRIOPIONATE | VALERIANATE |
|---|---|---|---|
| B. p. at 10 mm. | 120° | 110° | 130 |
| Sp. gr. at 15.5° | 0.966 | 0.979 | 0.955 |
| Ref. index at 20° | 1.4638 | 1.4643 | 1.4630 |

## Terpinyl Acetate

Terpinyl acetate, $C_{10}H_{17}COO.CH_3$ is an ester which has a slight, but refreshing odour. It has scarcely any legitimate use in perfumery, but is manufactured and sold as an artificial ester to fraudulently add to terpenes, etc., to produce a mixture which is used for the adulteration of essential oils sold on their ester valve. Its detection is dealt with under "ester estimation" (*vide page* 604). Commercial terpinyl acetate should have the following characters:

Sp. gr. at 15.5°.............................. 0.955–0.966
Ref. index at 20° ........................... 1.4648 to 1.4660
True ester content ......................... 86 to 92%

## The Acetylenic Esters

A number of esters containing a triple linkage have, of recent years come into some prominence in synthetic perfumery. Of the best known is methyl heptine carbonate, of the formula $CH_3.(CH_2)_4.C \equiv C-COO.CH_3$. This is a colourless oil of specific gravity 0.952 at 15.5° and boiling at 107° at 20 mm. pressure.

Its odour is sharp and penetrating, but when diluted reminds one of violets, and is very useful in rounding off perfumes. It is prepared by distilling castor oil in a retort, which results in the formation of heptanal $CH_3.(CH_2)_5.COH$. This is converted into dichlorheptane by the action of phosphorus pentachloride. Dichlorheptane $CH_5.(CH_2)_5.CHCl_2$ is converted into heptine, $CH_3(CH_2)_4.C \equiv CH$ by the action of caustic alkali, and the latter into sodium-heptine, $CH_3(CH_2)_4.C \equiv CNa$, by the action of sodium. This is treated in ether with methyl chlorocarbonate, which results in the formation of the finished product. There are several homologous esters of perfume value prepared in a similar manner, notably the methyl, ethyl and amyl octine carbonates.

## (H) NITROGEN COMPOUNDS

Nitrobenzene $C_6H_5NO_2$, also known as *oil af mirbane* is an oil not occurring naturally, but produced on a large scale by the nitration of benzene. It possesses a coarse almond odour, and is only suitable for exceedingly cheap perfumery work, such as that of covering the somewhat objectionable odour of very cheap soap, boot polish, and similar preparations. Its characters are as follows:

Solidifying point (if quite pure) ....................... +5°
B. p. ................................................... 209°
Sp. gr. at 15.5°........................................ 1.2060
Ref. index at 20° ..................................... 1.5520

Nitrobenzene used to be found as an adulterant of essential oil of almonds, but as synthetic benzaldehyde is now produced at a low price, it has replaced nitrobenzene as an adulterant, as it is far more difficult to detect. If adulteration with nitrobenzene be suspected, the oil should be shaken in the usual manner with a hot

solution of sodium bisulphite (25–30%). According to Reclaire (*Perfumery and Essential Oil Record*, 1922, **356**), under 2% will fail to be detected. With 10% or over the estimation is approximately quantitative. With any quantity below 5%, the odour of the nitrobenzene becomes apparent after absorbtion, even though no undissolved oil remains.

Nitrobenzene can also be detected by reducing the oil in a little alcohol, with iron and acetic acid, when aniline is formed which is identified by the usual reactions.

J. E. Pickering has (*J. Chem. Soc.*, 1922, **70**, 144) stated that nitrobenzene yields a pink to red coloration when mixed with a dilute alcoholic solution of caustic soda. This, however, has been shown to be due to the presence of dinitro-thiophene, a fairly common impurity in samples of commercial nitrobenzene. When this substance is absent, however, the reaction is not yielded, and cannot therefore be relied upon.

### Artificial Musk

No treatise on essential oils and perfume materials would be complete without a fairly full account of those important commercial substances known as the artificial musks.

These substances are in no sense identical with any natural constituent of musk. They are the result of laborious researches on the substances which gave promise of having an odour resembling that of musk, which strangely enough, are practically always nitro-compounds. These artificial musks have an intense odour, not identical with, but generally resembling that of natural musk. If used in very minute quantities, a pleasant result is obtained, and the value of artificial musk to the perfumer is now very great. But if used to an excess, the resulting odour is objectionable, coarse and vulgar. The artificial musks of any importance may be grouped in three classes. (1) Hydrocarbon musk, (2) ketone musk, and (3) musk Ambrette.

Although there are numerous homologues of the typical substance of each class, many of which have a musk odour, it is only the type substance of each class which is a substantial article of commerce, and only these three will be described.

*Musk-xylene*, as it is usually termed in the trade, is tri-nitro tertiary butyl xylene, of the constitution

$$C.NO_2$$
$$(C_4H_9)C.\quad\quad CH_3$$
$$NO_2C\quad\quad CNO_2$$
$$CH_2$$
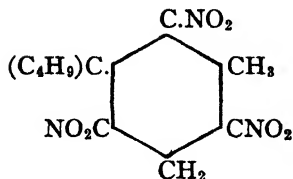
This substances is prepared by the condensation of isobutyl chloride and *meta*-xylene in the presence of aluminium chloride. An intramolecular change takes place, whereby the isobutyl radicle becomes converted into the tertiary butyl radicle. The resulting hydrocarbon is nitrated, and xylene musk results. This is a yellowish white crystalline substance melting at 111°–113°. It should be tested for acetanilide by the phenyl isocyanate reaction.

*Ketone-musk.*—If the acetyl group is introduced into the hydrocarbon molecule, and the methyl ketone thus formed is nitrated, ketone musk results    If butyl-xylene dissolved in carbon disulphide be condensed with acetyl chloride in the presence of aluminium chloride butyl-xylyl-methyl ketone results. This is nitrated, and the ditnitro derivative resulting has the following constitution:

$$C.CO.CH_3$$
$$(C_4H_9)C\quad\quad C.CH_3$$
$$NO_2C\quad\quad C.NO_2$$
$$CH_3$$
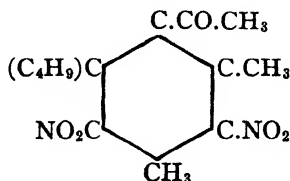
When quite pure this substance, known as ketone musk, melts at 136°. The corresponding ketone musk prepared from butyl-toluene melts at 131°, and as, unless recrystallised several times, the melting points may be a few degrees below those given, a sample of ketone musk should not be condemned because its melting point is a trifle lower than 136°, unless a foreign substance, such as acetanilide, can be detected.

*Musk-ambrette* is usually regarded as considerably the finest in odour of the artificial musks. It is made by building up from *meta*-cresol. This is esterified to *meta*-cresol methyl ether, which is condensded with isobutyl chloride, and the resulting pseudobutyl *meta*-cresyl ether is nitrated. The resulting dinitro-butyl-*meta*-cresol methyl ether has the following constitution

$$C.CH_3$$
$$NO_2C \quad\quad C.NO_2$$
$$CH_3.O.C \quad\quad C(C_4H_9)$$
$$C.NO_2$$
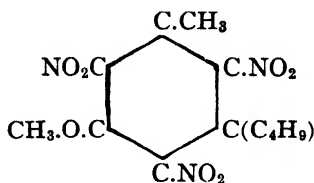
It melts at 85° when absolutely pure.

It must be borne in mind that there are a number of homologues of these three substances, as well as, incidentally, an aldehyde musk. Under the general name "artificial musk" it may well be that mixtures of these substances are sometimes offered in commerce. So long as no foreign substances such as acetanilide, etc., is present, no exception could be taken to this. But when artificial musk is sold under the names "musk-xylene," "ketone musk" or "musk ambrette," their composition is so well established by trade usage that, with the exception of the presence of small quantities of the corresponding homologues, no admixture is permissible.

### Indol and Skatol

Indol and skatol are two evil-smelling nitrogenous substances, both of which are found naturally, the former in neroli and jasmin oil and the latter in civet. When used in minute quantity, however, they impart characteristics to certain perfumes, which are invaluable to the perfumer, in the same way as minute quantities of asafœtida or garlic give a "je ne sais quoi" effect to many edible articles.

Indol is a crystalline compound melting at 52° and boiling at 254°. Its odour in the pure state is distinctly fæcal. Its constitution is as follows:

$$CH$$
$$HC \quad C \quad\quad CH$$
$$HC \quad\quad CH$$
$$C$$
$$CH \quad NH$$
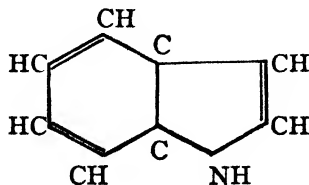
It is prepared artificially by numerous methods; the whole of the indol of commerce is artificial, as it would not be remunerative to extract it from natural sources.

Indol can be estimated in essential oil mixtures by mixing the sample with 10% of picric acid and heating to 60°. Excess of petroleum spirit is then added. A compound of picric acid and indol separates in long red crystals. These are washed with petroleum spirit, decomposed by caustic alkali, and the free indol extracted by ether, and the residue left on evaporation of the ether steam distilled, when pure indol passes over, and separates in crystals and can be weighed.

Indol dissolved in alcohol colours a pine wood shaving moistened with hydrochloric acid, a cherry red.

Skatol, $C_9H_9N$, is $\beta$-methyl indol of the constitution
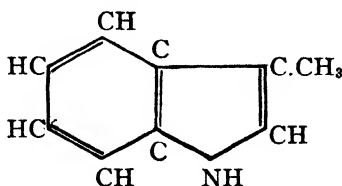


It forms crystals melting at 95° and boiling at 266°. It yields a hydrochloride melting at 167°–168° and a picrate melting at 172°–173°. With a solution of dimethyl-aminobenzaldehyde it yields a fine blue colouration.

It is never extracted from civet or other sources in which it is found naturally, but is manufactured artificially. It is used in minute quantity in the manufacture of flower perfumes.

## (I) Various Substances

These are a few substances not falling under the headings so far dealt with, which are of sufficient importance to be mentioned here.

These are coumarin, ascaridol, and phenyl-acetic acid.

### Coumarin

Coumarin $C_9H_6O_2$ is the $\delta$-lactone of coumarinic acid, having the constitution
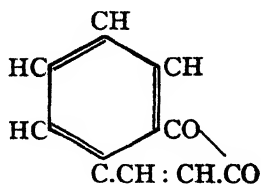
It is the predominating constituent of the Tonquin Bean (seeds of several species of Dipteryx), and also occurs in the leaves of the American plant known as the Deer's tongue (Liatris odoratissima). It is a perfume material of such general employment, that its artificial production is now carried on a considerable scale. Amongst the methods by which it can be prepared is that of Perkin (*J. Chem. Soc.*, xxi, **53**, 181) who prepared it by heating salicylic aldehyde with acetic anhydride and sodium acetate. By this reaction coumarin and aceto-coumaric acid are formed, the latter yielding coumarin on heating with water, so that on distillation, coumarin is the principal product.

Coumarin is largely employed in the manufacture of perfumes of the "new mown hay" type. It is a crystalline solid melting at 67°–68° and boiling at 290°.

### Ascaridol

Ascaridol is the chief constituent of the essential oil of *Chenopoduim Ambrosoides*. It is an oxide, of the formula $C_{10}H_{16}O_2$, but whose constitution is still a matter of doubt. It has the following characters:

Sp. gr. at 15.5° .................................... 1.000
Opt. rot. .......................................... −4° 14'
Ref. index at 20° ................................... 1.4731
B. p. at 5 mm. ..................................... 83°

According to Nelson its constitution is



$$CH.CH_3$$
$$H_2C \quad\quad C$$
$$O^O$$
$$HC \quad\quad CH$$
$$CH.CH.(CH_3)_2$$
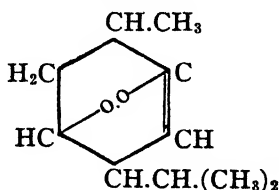
### Phenyl-acetic Acid

This substance, $C_6H_5.CH_2.COOH$, is found in neroli oil and otto of roses. It has a sweet honey-like odour, and is coming into some vogue in synthetic perfumery. It is a crystalline solid melting at 76°–76.5° and boiling at 266°. It is prepared by digesting benzyl cyanide with dilute sulphuric acid.

# THE GENERAL CHARACTERS AND ANALYSIS OF ESSENTIAL OILS

## By E, J. PARRY

The great majority of the products known as *essential oils* are proximate principles occurring in nature ready-formed, or as glucosides which by the action of water or enzymes readily undergo decomposition into essential oils and one or more other substances. The characteristic odours of plants are due, in nearly every case, to the presence of essential oils.

Broadly speaking, the essential oils differ from the fixed or fatty oils by being volatile without leaving any fixed residue. Hence they do not produce a permanent, translucent, oily mark on paper. In most cases also the essential oils possess strong and characteristic odours. For general purposes this distinction is sufficient. But it must be remembered that many essential oils are mixtures of a preponderating amount of constituents which are volatile without decomposition, together with a certain amount of fixed non-volatile matter which has either been mechanically carried over in the distillation (such as is the stearoptene of otto of rose), or which results from the oil having been prepared by expression (as in the case of bergamot oil). Further, although most essential oils are volatile without decomposition, many cannot be distilled under ordinary pressure without some decomposition occurring, and must therefore be distilled under reduced pressure or in a current of steam.

### Extraction of Essential Oils

The volatile oils of plants are obtained:

(*a*) By expression, as the oils of lemon and bergamot.

(*b*) By *distillation with water*, or by passing a current of *steam* through the matter to be extracted. This is the most common and generally applicable method.

(*c*) By *fermentation and distillation;* as, for instance, with the essential oils of mustard and bitter almonds, the seeds containing no ready formed essential oil, the latter being produced when the

crushed seeds are left in contact with water, owing to the influence of peculiar nitrogenised ferments, the oil formed being then separated by distillation with water.

(d) By *solution in a fixed oil* devoid of odour, such as olive oil, lard, or hydrocarbon oil (the "enfleurage" process). The perfumes of the more delicate plants are extracted in this manner, such as the violet, cassie, and tuberose.

(e) By *extraction with a volatile solvent* and recovery of the volatile solvent by distillation. This process is only used in the case of delicate oils which may not be exposed to high temperatures and the resulting perfume material is usually sold as a concrete, and not as a definite essential oil.

Many of the oxygenated and sulphuretted constituents of essential oils have been prepared artificially.

## Composition of Essential Oils

Essential oils as may be judged from the preceding pages, are usually of very complex composition, and different specimens from the same botanical source often exhibit considerable variations in the proportions of their constituents. These variations are due to many external conditions, such as climate, soil, method of cultivation, etc. A leading example of such a variation may be found in plants of the Labiate family, such plants as peppermint or lavender yielding entirely different oils according to the district in which they are cultivated. An English lavender oil will be found to contain less than 10% of esters, whereas if the same plants be transplanted to France the ester value of the oil will gradually increase up to 35% or more. The age of the plant is also an important factor in the composition of an essential oil, as the same plant gathered when immature and when ripe may yield quite different essential oils.

The only satisfactory classification of essential oils is according to their botanical origin. The alternative method, adopted by many French chemists, is to classify them according to their chemical relationships. But this at once raises a serious difficulty. Many oils owe their chief characteristics to at least two different substances. For example, citronella oil contains a large amount of both geraniol and of citronellal. If we adopt a chemical chassification, are we to place this oil with otto of rose, which contains a very large amount of geraniol, or with a lemon-grass oil, which consists chiefly of the

aldehyde, citral.  Both German and English chemists prefer a botanical classification, and this will be found to have considerable advantages over a chemical one.   The greater part of the essential oils will be found to owe their principal characteristics to one or more of the following groups of compounds:

1. *Terpenes*, hydrocarbons of the formula $C_{10}H_{16}$: in many of these cases 90% of terpenes are present, but they are seldom the most useful portion of the oil, which frequently depends entirely for its value on the remaining consitutents, *e. g.*, lemon oil, orange oil.

2. *Sesquiterpenes*, hydrocarbons of the formula $C_{15}H_{24}$: cedarwood oil and patchouli oil are types of this class.

3. Open-chain *alcohols* and their corresponding *aldehydes:* such are the so-called Indian grass oils (citronella, lemon-grass and Indian geranium oils).

4. *Aromatic alcohols* of the *Camphor series* and their corresponding ketones, such as peppermint, thuja, and pennyroyal oils.

5. *Aromatic alcohols* of the *Benzene series* and their corresponding *aldehydes* and *ketones*, such as bitter-almond oil, caraway oil, and cinnamon oil.

6. *Sesquiterpene alcohols*, such as sandalwood oil.

7. *Phenols* and their derivatives, such as clove and aniseed oils.

8. *Esters* of any of the above-mentioned alcohols, such as lavender and bergamot oil, wintergreen oil.

9. *Sulphur compounds*, such as garlic oil.

There are a few oils which do not come under any of these heads, but they are not very numerous.

## General Characters of Essential Oils

The essential oils of plants are usually liquid at ordinary temperatures, but many of them deposit solid substances, called *stearoptenes*, by sufficient cooling, *e. g.*, camphor, and the paraffin hydrocarbons of rose oil.   The essential oils have marked, and in most cases characteristic, odours.   They volatilise slowly at ordinary temperatures, though their boiling points are mostly somewhat high.   Essential oils are usually colourless or yellow when freshly prepared, but a few have well-marked colours.   Some oils darken rapidly on exposure to air and light.   Oils which contain aromatic aldehydes often deposit crystals of the corresponding acids on exposure to air.

Those volatile oils which consist chiefly of terpenes are very prone to change in contact with air and moisture, especially in presence of light.    The chief products of such change are ill-defined resinous substances, the chemistry of which is but little understood.    There is no evidence of the conversion of the hydrocarbons into any of the normal odorous constituents of such oils.    On the contrary, Charabot has adduced evidence that, in some cases, the terpenes result from the dehydration of preformed alcohols, during the development of the plant.[1]

Most of the essential oils are optically active.    In a number of cases the rotatory power only varies between well-defined limits, so that this character is of great valueami in the exnation of the oils.

All essential oils possess somewhat high refractive indices.    Taken at 20°, this figure will be found to vary from about 1.4600 to 1.5100, with a few oils outside these limits.    For example, oil of rue has a refractive index of about 1.4350, while oil of bitter almonds reaches 1.45560.    The value of optical methods for essential oils cannot be overestimated, but their limitations must be recognised.    If a given sample shows values which are outside the well-established limits, adulteration may be presumed, but oils may easily be adulterated skilfully so that they will show the same values as those for pure oils. Hence, when the values are within prescribed limits, they must only be taken as confirmatory.    It must be remembered, too, that the optical values found are the mean of those of numerous optically active constituents, and an optically inactive oil may consist of a number of dextrorotatory and lævorotatory substances so balanced as to produce an optically inactive mixture.    The separation of an oil into fractions by distillation under reduced pressure is essential in many investigations.    The optical characters of the various fractions will, in the hands of a skilled operator, indicate much that is not suggested by the observation of the optical characters of the oil itself.

The specific gravities of the essential oils mostly range between 0.850 and 0.990; but some few have a specific gravity below 0.850, such as oil of hops (0.840), while others are considerably heavier than water, such as oil of wintergreen (1.187).    The specific gravities

[1] Charabot considers that the formation of the chief constituents takes place in 2 stages, the first of which determines the elaboration of alcohols, which by the elimination of water or by esterification are converted into terpenes and esters, respectively.    The second stage he regards as coincident with the period during which the respiratory energy is brought to bear on the processes of assimilation, when the quantity of oxygen fixed is sufficient to convert the primary alcohols into aldehydes and the secondary into ketones.

of some essential oils are liable to variations with the age of the samples and other conditions.

The essential oils are all readily combustible. They are in most cases insoluble, or nearly so, in water, but distinct traces of some of them pass into solution, the water acquiring the characteristic taste and odour of the oil.[1]   In alcohol they are freely soluble, and are reprecipitated from their solutions by dilution with water.  The separation, however, is rarely, if ever, complete.  The essential oils are miscible in all proportions with fixed oils, oil of turpentine, light petroleum, and carbon disulphide, and may be separated from aqueous liquids by agitation with these solvents.

On cooling natural essential oils, the solid principles forming the stearoptenes often crystallise out.[2]   On distilling an oil thus freed from substances of high melting point the more volatile hydrocarbons first pass over, and on raising the temperature the remainder of the stearoptene may also be obtained in some cases, the non-volatile residue consisting either of non-volatile solid matter which has been carried over mechanically in the original distillation, or of products of oxidation of the oil, frequently of a resinous nature.  The more volatile portion of the distillate may be freed from oxygenated compounds by redistillation over sodium, and the hydrocarbons, when present, thus obtained pure.

It is to the presence of oxygenated constituents that the character-istic aroma, flavour, and medicinal value of most essential oils are chiefly, if not entirely, due, the hydrocarbons having but little value in these respects and acting chiefly as diluents.  Hence so-called "terpeneless" or "concentrated" essential oils are now pre-pared by careful fractional distillation of the crude oils.  The terpenes have a lower boiling point than the valuable alcohols, aldehydes, etc., and hence pass over first, while the fractions of higher boiling point are more powerful in odour and flavour than the entire oil, owing to the removal of the greater part of the com-paratively valueless terpenes.[3]

Since the value of the oxygenated constituents of essential oils has become more generally recognised, methods for estimating the pro-

[1] Dragendorff states that 1 litre of water holds in solution the following quantities of essential oils: Oil of cloves, 1.5 grm. oil of rosemary, 0.9; oil of lavender, 0.5; oil of pepper-mint, 0.2; oil of savin, 0.5; oil of copaiba, 0.12; and oil of bitter-almonds, 2.2 grm.
[2] Schimmel & Co. (Report, Oct., 1898) employ a modification of Beckmann's freezing-point apparatus for the determination of the solidifying-point of the oils of anise, fennel, etc.
[3] By careful fractionation, lemon oil can be separated into about 94% of terpenes and 5% of oxygenated compounds (chiefly citral and esters of geraniol).  The distillation is necessarily conducted under reduced pressure, since too high a temperature leads to decomposition of some of the oxygenated constituents.

portion present in the oils and of isolating some of them in an aproximately pure state have come into use, and certain of them have received official recognition in the pharmacopœias of recent date. These analytical methods are described at length in the sequel.

## Analysis of Essential Oils

The isolation or estimation of the various constituents of essential oils is often extremely difficult, and not infrequently impossible. Much advance, however, has been made in this direction of late years, and though no generally applicable or systematic method of analysis can be prescribed, in many cases it is now quite feasible to ascertain by comparatively simple methods the presence and approximate proportion of the constituent on which the value of an essential oil depends. Thus, by agitating the oil with a 5% solution of alkali hydroxide, the phenols in such oils as clove and thyme can be approximately estimated. By boiling with alkali hydroxide in alcoholic solution, any *esters* will undergo saponification. Boiled with sodium hydroxide and lead acetate, the *sulphuretted oils* (e. g., oils of garlic and mustard) give black lead sulphide. Oils containing aromatic *aldehydes* precipitate metallic silver from an ammoniacal solution of the nitrate. The aldehyde may be approximately separated from the other constituents by agitating the oil with a strong aqueous solution of sodium hydrogen sulphite, when (1) a crystalline compound is formed from which the remaining oil may be separated by agitation with ether; or (2) the crystalline aldehyde-sulphite compound dissolves in the excess of sulphite solution, and the lighter non-aldehydic portion of the oil may be readily separated from the lower aqueous layer.

The foregoing classes of constituents having been separated as completely as possible, the chemically indifferent compounds can then be more advantageously dealt with.

**Fractional distillation** affords one of the simplest and best means of effecting a rough proximate analysis of essential oils. The process should be conducted systematically, and under conditions as little variable as possible. The use of a Wurtz flask is generally sufficient to separate the necessary fractions, but it is undesirable to prolong the operation of distillation longer than is absolutely necessary, since

polymerisation or other change is liable to occur by long exposure to a high temperature.

In the analysis of essential oils and allied substances, it is frequently necessary to distil the liquid under examination at a reduced
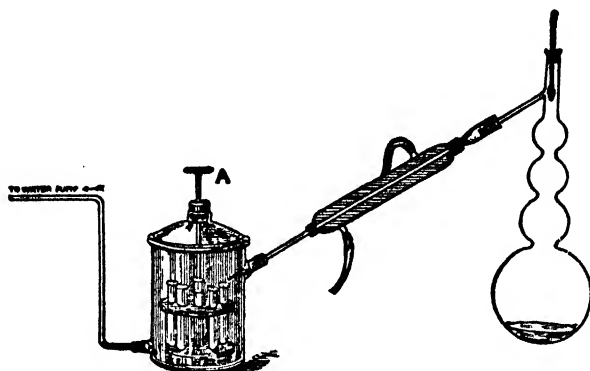


FIG. 7.
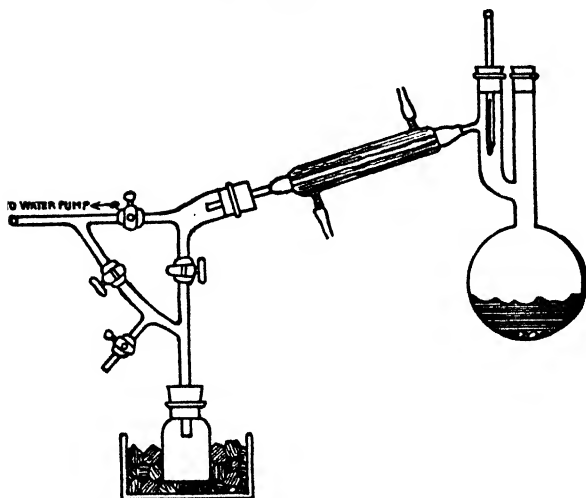


FIG. 8.—Apparatus for distillation under reduced pressure.

pressure, or even *in vacuo*, or by means of a current of steam. For example, in the estimation of the citral in lemon oil by Parry's process, the oil must first be concentrated by distilling off the greater part of the terpenes at a pressure of about 12 mm. In the

apparatus shown in Fig. 7 the distillate drops into a series of test-tubes which can be revolved at will by turning the handle A of the Brühl's jar, without breaking the vacuum.

An alternative form of apparatus (Fig. 8) is that recommended by Fischer and Harries (*Ber.*, 1902, **35,** 2158). The glass-tube triangle, fitted with four stop-cocks, enables the receiver to be changed by letting in air to equalise the pressure, without destroying the vacuum in the apparatus. This arrangement is also more convenient than a Brühl's jar, which takes some time to exhaust.

### Detection of Sulphur Compounds in Essential Oils

Sulphuretted substances, such as form the major parts of the oils of garlic and mustard, may be detected by boiling the sample with lead acetate solution and excess of sodium hydroxide, when black lead sulphide will separate.

For the detection of iso-thiocyanates or thiocarbimides, such as exist in oil of mustard, the sample should be boiled with alcoholic sodium hydroxide, the solution diluted with water, acidified with hydrochloric acid, and a drop of ferric chloride added. The production of a blood-red colour, due to the formation of ferric thiocyanate, indicates the previous existence of an isothiocyanate (thiocarbimide).

**General Plan of Analysis.**—As a rule, the problem with which the analyst is confronted is not to deal with a totally unknown type of essential oil, but to decide on the purity and value of an oil of a known type. This being the case, any general scheme of analysis must necessarily be modified to meet the given conditions.

The specific gravity of essential oils varies within comparatively narrow limits in most cases, although in a few the variations are very wide. The determination of this and other physical characters are therefore of the utmost importance; and the figures for the specific gravity, optical rotation, and refractive index will sometimes indicate whether a given oil is pure or not. In general, the physical characters can be so nicely balanced by a skilled adulterator that it is not difficult to make mixtures having the physical characters of a genuine oil. It is here that the value of fractional distillation comes in. If the oil be distilled, either at ordinary or at reduced pressure as the case may require, and the temperatures of the

various fractions noted, and then the physical characters of the fractions taken, it will be found very difficult to imitate such a combination of figures. For example, a pure oil of peppermint, having a refractive index 1.4645, will, on distillation at reduced pressure, give fractions the refractive indices of which vary from 1.4600 to 1.4660, until the last 10% residue, which will have a refractive index about 1.4780 to 1.4790. The recent use of triacetin as an adulterant of this oil was detected by the indications afforded by this last 10% of the oil on distillation, when the refractive index was found to be 1.4436, so low as to point at once to adulteration with a substance of low refractive index and high b. p. Again in the case of another recent adulterant of this oil, the last fractions were found to have refractive indices up to 1.4900 to 1.4980. This figure at once suggests a substance of the sesquiterpene or phenolic type. As a matter of fact it was found to be the sesquiterpene oil of African copaïba. Such considerations demonstrate the necessity of examining the physical characters of the fractions of the oil rather than to place too much reliance on those of the oil itself.

The determination of the physical characters should be followed by the necessary quantitative valuations. These include (according to the type of oil) the estimation of 1. free acids; 2. phenols; 3. alcohols; 4. esters; 5. aldehydes and ketones. The general principles of these processes will now be described.

## Estimation of the Free Acids in Essential Oils

The acids may be estimated rapidly and with considerable accuracy by dissolving a known weight of the essential oil in neutral methylated spirit, adding a few drops of phenolphthaleïn solution, and titrating the liquid with standard alkali hydroxide. The operation may be carried out exactly as in the case of fixed oils.

1 c.c. of normal sodium hydroxide requires for neutralisation:

> 0.060 grm. of acetic acid.
> 0.102 grm. of valeric acid.
> 0.122 grm. of benzoic acid.
> 0.148 grm. of cinnamic acid.
> 0.138 grm. of salicylic acid.

The estimation of free hydrocyanic acid in essential oils is at times required in the examination of commercial samples.    L. W. Andrews (*Amer. Chem. Jour.*, 1903, **30**, 187) described a volumetric method which was based upon the interaction of hydrocyanic acid and mercuric chloride according to the equation $2HCN + HgCl_2 = Hg(CN)_2 + 2HCl$.    The free hydrochloric acid generated by the interaction is titrated with $N/10$ potassium hydroxide solution, *p*-nitro-phenol being used as the indicator.    The difficulty of this method lies in Andrews' directions that, after being diluted with mercuric chloride solution, the liquid has to stand for an hour.    Another drawback is the want of clearness in the colour-change of the nitrophenol. According to Rosenthaler (*Arch. Pharm.*, 1910, **248**, 529) the end-point may be more easily observed if iodoeosin is employed as indicator.    Rosenthaler also found that the result was equally satisfactory if the action was limited to a short time.

The following are required for the titration:

(1) $N/10$ potassium hydroxide solution and $N/10$ sulphuric acid.

(2) Iodoeosin (in 0.2% of alcoholic solution) and ether.

(3) Solution of mercuric chloride.

The estimation is carried out as follows: The liquid under examination, which should contain about 1% of hydrocyanic acid, should be diluted with iodoeosin solution, neutralised with alkali or acid until the solution just shows a pink tinge; mercuric chloride solution is added, and the mixture titrated back immediately with alkali, until the colour reappears.

Whether enough mercuric chloride solution has been added is shown by the titrated liquid no longer becoming coloured after the addition of a few drops of this solution.    If a colour should appear it is necessary to add more mercuric chloride and to titrate again with potassium hydroxide solution.    If there has been over-titration, add an excess of acid and titrate back again.    1 c.c. $N/10$ potassium solution = 2.7018 mg. hydrocyanic acid.

The estimation of the total hydrocyanic acid in liquids which contain free hydrocyanic acid and benzaldehydecyanhydrin offers no difficulties.    Neutralise with iodoeosin, dilute with excess of $N/10$ potassium hydroxide solution and again shake for 1 minute. Then add acid until decolorisation has been reached and titrate with alkali until the process is completed.    In all cases where solutions of unknown strength are concerned, it is advisable, after

finishing the titration, once more to add the potassium hydroxide and mercuric chloride solutions, and after allowing the mixture to stand for 5 minutes, to titrate again.    The calculation is based upon the following equations:

$$HCN + KOH = KCN + H_2O$$
$$C_6H_5CH(OH)CN + KOH = KCN + C_6H_5CHO + H_2O$$
$$2KCN + HgCl_2 = Hg(CN)_2 + 2KCl$$
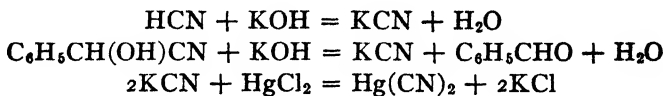
When free hydrocyanic acid has to be estimated in the presence of benzaldehydecyanhydrin it is not sufficient to dilute the neutralised solution with mercuric chloride and to titrate with alkali, because in that case the results are always too high, inasmuch as the nitrile is decomposed by the alkali as the latter is added.    In such a case the best mode of procedure is as follows:

The solution under examination is allowed to run into a separating funnel with about 20 c.c. of saturated neutral sodium sulphate solution and neutralised after adding 50 c.c. of ether and 10 drops of iodoeosin solution.    Any sodium sulphate which may be precipitated is re-dissolved by adding water.    Mercuric chloride solution is next added, the mixture vigorously shaken, and the aqueous liquid separated into a beaker.    The solution remaining in the funnel is then extracted once with 20 c.c. of sodium sulphate solution, and again with only a little of the solution.    The extracted acid is titrated in the usual way with alkali.

Viehover and Johns (*J. Amer. Chem. Soc.*, 1915, **37,** 601) give the following method for the estimation of hydrocyanic acid.    The acid is distilled over in a little water, and sodium hydroxide added to give a faint alkaline reaction.    The liquid is then concentrated *in vacuo* at a temperature of 70°, and when the volume is reduced to about 1 c.c., a few drops of a freshly prepared 3% solution of ferrous sulphate are added and about 50 mg. of potassium fluoride. In about 10 minutes the mixture is rendered slightly acid with dilute nitric acid (30%), when the blue colour appears at once. If only minute traces are present, it is necessary to warm the solution to 50° in order to develop the colour.    The colour is then matched by "Nesslerising," against a standard solution of potassium cyanide.    It is claimed that this process will give accurate indications to 100th part of a mg.

## Estimation of Alcohols in Essential Oils

Many essential oils contain free alcohols, often to so great an extent as to owe practically the whole of their odorous characters to them. Sandalwood, peppermint, rose, and geranium are types of oils rich in free alcohols.

No practicable method of actually separating these alcoholic substances exists, and their estimation must be regarded as approximate. So long as the estimation is carried out with care and under uniform conditions, however, the results are strictly comparable, when the following process is employed. The alcohols in the oil are converted into acetic esters, and a known weight of the acetylated oil is saponified by a solution of potassium hydroxide in alcohol. The actual estimation made is, of course, the amount of potassium hydroxide used for the saponification. From this the amount of a given alcohol can easily be calculated; it is therefore necessary to calculate the amount of free alcohols in terms of the predominating one present, such, for example, as geraniol in geranium oil. Although it is true that, in general, the free alcohols in an essential oil consist of a mixture of more than one compound, these are usually of nearly the same formula, so that a calculation in terms of one of them is approximately true for them all. It is obvious that no estimation of a mixture of geraniol, $C_{10}H_{18}O$, and a sesquiterpene alcohol could afford any basis for an accurate calculation.

Before describing the process usually adopted, it is necessary to point out that certain other substances react with acetic anhydride, and yield saponifiable esters. Such, for example, is citronellal, which is converted into isopulegyl acetate by acetylation; so that the amount of "free alcohols", as estimated by acetylation in citronella oil, in reality represents both the alcohols and the citronellal. Again, certain alcohols are partially decomposed during the process, and the results obtained are far below the truth. Such are the alcohols terpineol and linalol. In order to obviate this difficulty, Boulez recommends diluting the oil containing such alcohols with 5 times its weight of pure turpentine, and acetylating with about 8 times its weight of acetic anhydride. A blank experiment with only the oil omitted is necessary, and the proper deduction can thus be made. Although this does not give quite accurate

results, the dilution is a distinct advantage, and the results are not very far below the truth.

For normal cases, 10 c.c. of the sample are mixed with 15 c.c. of acetic anhydride and about 2 grm. of sodium acetate (anhydrous). The last-named is added to absorb the water liberated by the action, which would otherwise have a reversing effect on the esterification. The mixture is boiled in a glass flask, having a tube about 4 feet in length ground into its neck, during 2 hours. The high b. p. of acetic anhydride renders the glass tube an efficient condenser, and water cooling is not necessary. When the mixture is cold, it is well shaken with twice its volume of water in a separator, and when the layers have separated the water is run off. This is repeated 4 times or until the water contains no acetic acid. The acetylated oil is now allowed to stand for a short time on a little anhydrous sodium sulphate to remove traces of water, and, if necessary, filtered. For oils usually containing 70% or more of alcohols, about 2 grm. are used for saponification, while with oils containing only 15 to 20%, up to 5 grm. may be used. The acetylated oil, accurately weighed, is dissolved in a little alcohol, neutralised with N/10 alkali and boiled briskly with 25 c.c. of N/2 alcoholic potassium hydroxide under a reflux condenser for an hour, and the amount of alkali used is estimated in the usual manner by titration with N/2 acid.

Assuming that the original oil contains no esters or at most a negligible quantity, the calculations are simple enough, as the whole of the alkali used is employed for the saponification of the esters formed by the acetylation of the free alcohols. Remembering that the oil used for the saponification represents a smaller amount of the original oil, on account of its combination with the acetyl radical, the following formula will (in the case of ester-free oils) give the amount of free alcohols present:

$$P = \frac{M \times N}{10\,(W - 0.042\,N)}$$

where $P$ is the percentage of alcohol present, $M$ is its molecular weight, and $N$ is the number of c.c. of *normal* alkali used. The correction $0.042N$ is for the increase in weight of the oil due to acetylation. If the oil originally contains both esters and alcohols

these calculations will be useless.    In such cases it is necessary to proceed as follows:

1. Estimate the amount of combined alcohols by a preliminary saponification of the esters.

2. Saponify about 20 grm. of the sample with alcoholic potassium hydroxide solution, add water, and well wash the separated oil, now free from esters, dry over potassium hydrogen sulphate, and

3. Estimate the total alcohols (which are now all free) in 2 to 5 grm. of 2.

4. The amount of alcohols found in 3 refers, not to the original oil, but to the saponified sample; to calculate the total alcohols in the original sample a correction must be made by allowing for the reduction in weight by saponification of the original oil.    This reduction can be ascertained by calculation from the amount of alkali used for saponification in 1.

5. Deduct the combined alcohols found in 1 from the total alcohols found in 4.    This gives the amount of free alcohols.

It is assumed that the esters are uniform in molecular weight, usually as acetic esters.    This is not always accurate, as, for example, in peppermint oil, in which some of the esters are those of valeric acid. But the results are sufficiently accurate for all ordinary purposes.    In some oils the esters are principally those of higher acids; for example, in geranium oil where they are calculated to tiglic acid.

Power and Kleber (*Zeit. anal. Chem.*, 1894, **33,** 762), in describing the estimation of menthol in peppermint oil, give the following formula for calculation:

$$P = \frac{a \times 15.6}{s - (a \times 0.042)}.$$

where $P$ is the percentage of menthol (total), $s$ is the weight in grm. of the oil which has first been saponified and then acetylated, and $a$ is the number of c.c. of *normal* alkali used.

But an examination of this formula shows that $P$ is, in fact, calculated on the weight of the ester-free oil, and for strict accuracy requires the slight correction referred to above (No. 4).

Haller recommends the following modification of the above process in the examination of the oils of geranium, citronella, peppermint, etc.: The amount of esters is first separately estimated, and then a

separate portion of the oil is saponified with a suitable amount of potassium hydroxide, so as to obtain the whole of the alcohols in a free state.    The product is separated from the aqueous liquid, washed with water, and dried with anhydrous sodium sulphate.    The dried liquid is then heated either with succinic or phthalic anhydride, whereby the alcohols are converted into mono-ester acids.    Strong sodium hydroxide solution is then added to convert these compounds into sodium salts, and the terpenes and other indifferent substances are then removed by agitation with ether.    The pure alcohols are recovered by saponifying the alkaline liquid and extracting with ether.

The accurate separation of the open-chain alcohols from each other is attended with difficulty, and cannot in all cases be satisfactorily carried out.    The separation of geraniol and citronellol may be approximately effected by the following method of Flatau and Labbé (*Compt. rend.*, 1896, **122**, 1725):    The oil is saponified with alcoholic potassium hydroxide, and rectified *in vacuo*.    The portion distilling between 120° and 140° at 30 mm. pressure is dissolved, together with an equal weight of phthalic anhydride, in an equal volume of pure benzene.    After boiling the mixture for an hour under a reflux condenser the benzene is evaporated off, and the residue treated with sodium hydroxide.    The gelatinous mass thus obtained is dissolved in tepid water, and the solution shaken with ether to remove impurities.    The esters are then liberated by adding hydrochloric acid diluted with an equal volume of water, and washed out with petroleum spirit at about 25°.    The petroleum solution is then cooled to − 5°, when the *acid geranyl phthalate* separates out completely (in the course of a week) in well-formed crystals.[1]    On removing these and evaporating the mother-liquor, the *acid citronellyl phthalate* is left as a yellow oily residue which does not crystallise on cooling. The two esters thus obtained are then saponified separately with 5% alcoholic potassium hydroxide, and the liberated alcohols purified by re-distillation in a current of steam.

By the above process, Flatau and Labbé obtained the following percentages of open-chain alcohols from typical oils containing them:

[1] Geranyl phthalate crystallises in shining rhombic tablets which melt at 47°, and are readily soluble in the usual solvents in the cold, and in petroleum spirit at 25°.    It begins to separate on cooling its solution in petroleum spirit to about 10°, and is almost insoluble at −5°.    Silver geranyl-phthalate is a white powder melting at 133.8° (?138.8).    By treating geranyl-phthalate dissolved in ether with bromine, a tetrabromo-derivative is obtained melting at 114° to 115°.    These compounds may be employed for the identification of geraniol.

| Kind of oil | Total alcohols | Géraniol | Citronellol | Linalol |
|---|---|---|---|---|
| Indian geranium.............. | 80 | 63 | 17 | .......... |
| African (bourbon) geranium.... | 80 | 10 | 70 | .......... |
| Melissa..................... | 32 | 20 | .......... | 12 |
| Bulgarian rose ............... | 85 to 90 | 70 | 15 | .......... |
| Citronella ................... | 46 | 40 | 6 | .......... |

Schimmel & Co. state that the foregoing method is well suited for the preparation of pure geraniol, since the crystals readily separate and the alcohol obtained is as pure as that prepared by the calcium chloride method. On the other hand, the citronellol is always impure, owing to geranyl phthalate being not wholly insoluble in petroleum spirit. Hence the method is not suited for the quantitative estimation of the two alcohols in essential oils. To the inaccuracy of the method Schimmel & Co. attribute the detection of 17% of citronellol in palmarosa oil, a product which they assert contains mere traces, if any, of that substance.

According to Tiemann and Schmidt (*Ber.*, 1896, **29,** 903), the following method of detecting and estimating citronellol in admixture with geraniol gives very satisfactory results:

A solution of 100 parts of the sample under examination in 100 parts of absolute ether is cooled and added very gradually to a solution (cooled to −10°) of 60 parts of phosphorus trichloride in 100 parts of ether. During this operation the temperature must not be allowed to rise above 0°. The mixture is allowed to stand for 4 or 5 days at the ordinary temperature, and is then poured out on crushed ice, the ethereal layer washed several times with ice-water and agitated vigorously with dilute sodium hydroxide solution, which extracts from it citronellol (in the form of a chlorinated phosphorus ester acid), leaving behind geranyl chloride, etc. The alkaline solution is shaken once or twice with ether to remove impurities, rendered strongly alkaline, and steam-distilled in order to separate the liberated citronellol. The yield of citronellol is quantitative from samples containing not less than 20% of geraniol. Dextrocitronellol may be readily prepared in this way from citronella oil, which is first treated with sodium-amalgam in order to reduce the citronellal present, and the above process directly applied to the resulting mixture of alcohols.

The following figures are given by Tiemann and Schmidt as illustrating the application of the process to different oils:

|  | Total alcohols, % | Per 100 parts total alcohols | |
|---|---|---|---|
|  |  | Geraniol | Citronellol |
| Turkish rose oil..................... | 80 | 65 | (l—) 25 |
| Spanish geranium oil................. | 70 | 65 | (l and d) 35 |
| African geranium oil................ | 75 | 80 | (d and l) 20 |
| Réunion geranium oil................ | 80 | 50 | (d and l) 50 |

The citronellol from Réunion oil apparently contained traces of linalol. The so-called *réuniol* obtained by Hesse from the same source was found to be a mixture of geraniol with dextro- and lævo-citronellols, the latter modification predominating.

The method of acetylation, which is applicable to the estimation of the alcohol geraniol in a large number of oils, fails in the case of oil of citronella, as has been indicated above, since the isomeric substance citronellal, present therein in considerable proportion, is by treatment with acetic anhydride converted quantitatively into the acetic ester of isopulegol. Hence the result will be a measure of the geraniol of the oil *plus* the citronellal present. Formerly, the figure so obtained was taken as the criterion of value of citronella oil, but Schimmel & Co. (*Report*, Oct., 1899) have proposed a method by which the actual geraniol present can be estimated, while the difference between the amount found and the result of the acetylation process gives the citronellal of the sample. Schimmel's method is based on the conversion of the geraniol into its acid phthalate by treatment with phthalic anhydride, which has no action on citronellal. Secondary alcohols, like borneol, are scarcely attacked; while tertiary alcohols, such as linalol and terpineol, are wholly unaffected. Schimmel & Co. recommend that to 2 grm. of the oil under examination about 2 grm. of phthalic anhydride should be added, together with 2 c.c. of benzene, and the mixture heated on a water-bath for 2 hours in a flask furnished with a reflux condenser. After cooling, the mixture is shaken for 10 minutes with 60 c.c. (carefully measured) $N/2$ alkaline hydroxide solution, the flask being kept closed by a glass

stopper. By this treatment the excess of phthalic anhydride is converted into potassium (or sodium) phthalate, and the acid geranyl phthalate into a neutral compound. The excess of alkali is then titrated back with $N/2$ sulphuric acid. The difference between the volume of standard acid required and that of the alkali originally employed is equivalent to the phthalic anhydride which has reacted with the geraniol. Thus 1 c.c. deficiency of normal alkali represents 0.148 grm. of phthalic anhydride ($C_8H_4O_3$), or 0.154 grm. of geraniol ($C_{10}H_{18}O$).

In all acetylation processes, comparable results can only be obtained so long as the conditions of the estimation are kept constant. It should also be remembered that commercial acetic anhydride is somewhat variable in quality and only the purest available should be employed. But even in high grade acetic anhydride, traces of acetyl chloride are sometimes present, and this impurity appears to have a marked effect on the acetylation results. According to Salamon (*Perfumery and Essential Oil Record*, 1922, 357), the presence of acetyl chloride as found in commercial specimens will often make as much difference in an estimation as from 2 to 3%, calculated as geraniol.

The estimation of geraniol and citronellol as such when they are found together is a matter which is often of considerable importance. The fact that anhydrous formic acid abstracts water from geraniol whilst it converts citronellol into formates was first taken advantage of by Walbaum and Stephan (*Ber.*, 1900, 33, 2307) as a method for estimating citronellol in the presence of geraniol. The total alcohols are estimated by an acetylation, and the citronellol estimated by formylation, the geraniol being arrived at by the difference figure.

This method has been shown to be unreliable, but as it has been reported upon somewhat prominently, it is necessary to discuss its shortcomings. Too low values have been recorded, but these appear to be due to the use of weak formic acid. A. St. Pfau (*J. pr. Chem.* 1921, 102, 276) has examined the subject very critically. For the purposes of checking the value of the process he used three specimens of citronellol prepared by the reduction of citronellal from Java citronella oil or from citronellal-glycol. These three specimens had the following characters:

|  | 1 | 2 | 3 |
|---|---|---|---|
| B. p.................... | 105° at 7.5 mm. | 100° at 6 mm. | 107° at 8 mm. |
| Sp. gr. at 15.5°......... | 0.8658 | 0.8608 | 0.8628 |
| Opt. rot............... | +3° 5' | +3° 22' | +2° 52 |
| Ref. index at 20°........ | 1.4605 | 1.4593 | 1.4585 |
| Molecular refraction..... | 49.46 | 49.64 | 49.44 |

10 c.c. of citronellol were heated with 20 c.c. of formic acid for an hour, cooled, diluted with 100 c.c. of water, washed until neutral and dried over sodium sulphate, and then saponified. The results varied from 85% to 117% of citronellol.

St. Pfau concludes the high figures found in this estimation are due to the formation of citronellol glycol-diformate, and that the formylation process is unreliable.

C. T. Bennett (*Perfumery and Essential Oil Record*, 1921, 351) has also carefully examined the subject and comes to the same conclusion, so that the formylation process may be regarded as being quite unreliable for the separation of geraniol and citronellol in mixtures of the two substances.

Several methods have been proposed for the estimation of the amount of geraniol in the presence of citronellal, in, for example, citronella oil. All such methods are only approximate, but are useful where comparative results are required.

The phenylhydrazine method of Kleber is as follows. About 1 grm. of citronella oil (Ceylon type) or 0.5 grm. (Java type) is mixed with 10 c.c. of freshly prepared 2% alcoholic solution of phenylhydrazine. The mixture is allowed to stand in a closed flask for 1 to 2 hours and then 20 c.c. of decinormal hydrochloric acid solution is added and the mixture well skaken. Ten c.c. of benzene is then added and the mixture allowed to stand in a separator. The acid layer, which should measure 30 c.c., is filtered and 20 c.c. of the filtrate titrated with decinormal alcoholic potash, with the use of methyl or ethyl orange as indicator. The amount necessary for the 30 c.c. is calculated from this and the usual correction for a blank experiment is deducted. Each c.c. of decinormal potash used represents 0.0154 grm. of citronellal.

The oximation process, due to Dupont and Labaune, depends on the fact that citronellal forms an oxime when shaken in the cold with a solution of hydroxylamine. This oxime is converted on heating with acetic anhydride into a nitrile, which is not affected by boiling with alcoholic potash. Ten grm. of hydroxylamine

hydrochloride are dissolved in 25 c.c. of water. Ten grm. of potassium carbonate are dissolved in 25 c.c. of water and added to the other solution. The mixture is then filtered. Ten grm. of the oil are then shaken with this solution for two hours at ordinary temperature. The oil is then separated, dried over anhydrous sodium sulphate, acetylated in the usual manner, washed, dried and saponified. The difference between the total acetylisible constituents, and the value so obtained, is a measure of the citronellal content.

Boulez recommends shaking 25 grm. of the oil in an Erlenmeyer flask with 100 grm. of saturated solution of sodium bisulphite and sulphite. The mixture is allowed to stand for three hours with occasional agitation. About 100 c.c. of water are then added and the mixture heated under a reflux condenser for 2 hours, with frequent shaking until a clear oily layer separates on standing. The mixture is transferred to a separator, and the oil separated and measured. The loss approximately represents the amount of citronellal, and the geraniol is determined in the residual oil by acetylation.

Glichitch (*Comptes rend.*, 1923, 4, 268) has proposed to use a mixture of formic and acetic anhydrides for the esterification in the estimation of linalol, etc. One part of formic acid (sp. gr. 1.22) and 2 parts of chlorine-free acetic anhydride are mixed. Ten c.c. of the oil are used, with 15 c.c. of the mixture and the whole well shaken, placed on ice, and then allowed to attain room temperature, and remain thereat for 72 to 96 hours. The excess of acid is removed by shaking with water and washing with $NaHCO_3$ solution, and the saponification carried out in the usual manner. The alcohols are said to be converted into formates, This, however, requires confirmation.

In practice several difficulties occur in estimating free alcohols in essential oils by acetylation methods. It is, of course, understood that in all cases when the alcohols actually exist as a mixture of two or more substances, the estimation is in fact only a calculation based on the amount of alkali used in saponification, the alcohols being returned in terms of the predominant constituent.

A difficulty occurs in the case of certain alcohols of which linalol may be taken as a type. This alcohol decomposes to a considerable extent under the action of acetic anhydride, so that the results obtained are considerably below the truth. In order to obtain

approximately accurate results, Boulez (*Bull. Soc. Chim.* [iv], 1907, **1**, 117) has recommended the following modification of the ordinary acetylation process. 5 grm. of the oil are diluted with 25 grm. of turpentine which has been carefully rectified over sodium, and then boiled with 40 c.c. of acetic anhydride and 3 to 4 grm. of anhydrous sodium acetate. A blank experiment is necessary in order to allow for the apparent alcohol value of the turpentine. This process gives results in the case of linalol which are considerably nearer the truth than with the ordinary acetylation process. Xylene gives even better results than turpentine.

It has been recognised by all workers on the subject that the acetylation process, whilst giving excellent results, varies to the extent of several per cent., according to the exact details of the process used. The following details have been therefore agreed upon by most chemists handling essential oils, so that comparative results may be always obtained.

10 c.c. of the oil are boiled under a reflux condenser with 15 c.c. of acetic anhydride and 2 grm. of anhydrous sodium acetate for 2 hours. The mixture is then thoroughly washed with brine until free acid is removed. The washed oil is allowed to stand in contact with anhydrous sodium sulphate for 1 hour with occasional shaking. It is then filtered and a weighed quantity, after exact neutralisation with N/10 alcoholic potassium hydroxide, saponified for 1 hour under a reflux condenser with an excess of alcoholic potassium hydroxide; the excess of the last-named should be about equal to the amount necessary for saponifying the acetylated oil.

## Estimation of Esters in Essential Oils

Esters in essential oils may be readily estimated by the saponification process of Koettstorfer employed for the examination of fixed oils. Certain modifications of the procedure prescribed for fatty oils are sometimes desirable, such as judicious alterations in the quantity of the sample and in the strength of the alkali used.

In certain cases, essential oils contain a small quantity of free acids, when, of course, a preliminary titration with N/2 alcoholic potassium hydroxide will be necessary, and a due allowance made for the acids. Esters such as linalyl acetate (in lavender and bergamot oils), geranyl tiglate (in geranium oil) frequently form the most important con-

stituents of essential oils. While different views are held as to the direct proportion between ester content and odour value in certain oils, such, for example, as lavender oil, in other cases it is quite certain that the odour value is in practically direct ratio to the ester value. This is true in the case of bergamot oil, which owes its perfume to the linalyl acetate present. Indeed, it may be accepted that where the ester is associated with no other compound of much odour value this holds good, but where, as in the case of lavender oil, there are numerous other substances contributing to the odour of the oil, the ratio between ester content and odour value is not direct.

Saponification of from 2 to 5 grm. of the oil under a reflux condenser for an hour, by boiling with 15 to 25 c.c. of alcoholic potassium hydroxide of approximately N/2 strength, and titration of the excess of alkali with N/2 sulphuric acid at once gives the percentage of esters, assuming that only a single ester is present. As a matter of fact, usually there are several esters present, often of different molecular weights, so that in practice the amount of alkali consumed is calculated to the predominant ester, such as menthyl acetate in peppermint oil, linalyl acetate in bergamot and lavender oils, and geranyl tiglate in geranium oil.

Thus 1 c.c. of normal alkali hydroxide represents:

> 0.088 grm. of ethyl acetate.
> 0.152 grm. of methyl salicylate.
> 0.196 grm. of linalyl acetate.
> 0.196 grm. of bornyl acetate.
> 0.198 grm. of menthyl acetate.

Although the estimation of esters in essential oils is of extreme value, considerable difficulty in correctly interpretating the results obtained has recently been introduced on account of the abuse of scientific knowledge which has led to the preparation of a series of artificial esters, most of which have a saponification value which would indicate the presence of considerably more natural ester than the actual amount of artificial ester used as an adulterant. The principal esters used in connection with these frauds are as follows: terpinyl acetate, glyceryl acetate, ethyl citrate, ethyl oxalate, ethyl succinate, ethyl tartrate, and ethyl phthalate. Apart from the actual identification of the acid constituents of these

esters, the following notes in regard to one or two of them will be of value.

**Terpinyl Acetate.**—This ester is principally found as an adulterant in oil of bergamot, oil of petitgrain, and similar essential oils. The natural ester present in this class of oil consists principally of linalyl acetate. Linalyl acetate is hydrolysed at a considerably more rapid rate than terpinyl acetate. It therefore becomes possible to state with certainty that an artificial ester, probably terpinyl acetate, is present in either of these oils when a marked difference is found between the saponification value as observed at 30 minutes, and that observed in 60 minutes. From the accompanying table[1] it will be seen that hydrolysis of linalyl acetate or of bergamot oil is practically complete in 30 minutes, whereas, the saponification of terpinyl acetate or of bergamot oil adulterated with this ester is much slower.

| Ester | Time of saponification, minutes | | | | | 2 hours |
|---|---|---|---|---|---|---|
| | 5 | 15 | 30 | 45 | 60 | |
| Linalyl acetate (Schimmel & Co.)............... | 191.5 | 217.5 | 223.2 | 223.7 | 223.1 | 224.7 |
| Terpinyl acetate.............................. | 108.2 | 166.8 | 209.7 | 233.4 | 245.8 | 262.7 |
| Bergamot oil................................. | 80.3 | 94.5 | 97.3 | 97.5 | 97.8 | 98.5 |
| Bergamot oil + 5 % terpinyl acetate........... | 82.5 | 94.8 | 101.2 | 102.1 | 104.7 | 107.2 |
| Bergamot oil + 10 % terpinyl acetate..... ...... | 79.9 | 96.4 | 102.8 | 105.2 | 108.3 | 112.5 |
| Bergamot oil + 25 % terpinyl acetate........... | 78.8 | 100.6 | 108.1 | 116.4 | 119.0 | 126.8 |

Small quantities of terpinyl acetate can be detected by a process of fractional hydrolysis. The following process devised by Messrs. Schimmel & Co., yields most accurate results. Three separate saponifications should be made, using about 2 grm. of oil for each test. 5 c.c. of alcohol are then added, and the free acid neutralised with $N/2$ potassium hydroxide solution. The first saponification should be made for 1 hour with 10 c.c. of $N/2$ potassium hydroxide; the second should be saponified for 2 hours with 20 c.c. $N/2$ alkali, and the third for 1 hour with 10 c.c. of $N/2$ potash and 25 c.c. of 95% alcohol. After saponification the flasks should be cooled quickly by immersion into cold water and titrated at once. In the case of pure oils such as bergamot, petitgrain and lavender, the difference between the saponification for 2 hours and for 1 hour with dilute potassium hydroxide solution will not be more than 3 or 4,

[1] *Schimmel & Co.'s Report*, Oct., 1910, page 60.

whereas, if terpinyl acetate be present, as little as 2% will cause the difference to be from 6 to 7, and 5% will raise it to about 12.

**Ethyl Citrate.**—Essential oils adulterated with ethyl citrate show a marked turbidity at the commencement of the saponification process.    This is due to the separation of potassium citrate which is sparingly soluble in alcohol.    After boiling for some time, this turbidity may disappear.    Pure bergamot or similar oils do not show this turbidity.

The following method of identifying citric acid is due to Denigés: (*Bull. Soc. Ph. Bordeaux,* 1898, 33).    10 c.c. of the saponification liquor from which the separated oil has been removed, are shaken with 1 grm. of lead peroxide, and 2 c.c. of solution of mercuric sulphate of about 5% strength.    After vigorous shaking the liquid is filtered and 5 c.c. of the filtrate heated to boiling point, and a 2% solution of potassium permanganate added drop by drop, constantly stirring until it ceases to become immediately decolorised.    If citric acid is present a flocculent pale yellow or white precipitate develops after the first drop.

**Glyceryl Acetate.**—This adulterant is usually a mixture of glyceryl acetates in which triacetin predominates.    Its detection is moderately easy on account of the fact that it is readily soluble in very dilute alcohol, and even fairly soluble in water.    Messrs. Schimmel & Co. (*Half-yearly Report,* Oct., 1910, 61, and April, 1911, 150) have proposed the following methods for its detection.

10 c.c. of bergamot oil are mixed in a separating funnel with 10 c.c. of light petroleum and 2.5 c.c. of alcohol, and vigorously shaken up with 20 c.c. of water.    The addition of light petroleum and alcohol causes a very rapid separation of the oil and the aqueous liquid, so that the latter can be filtered off when the mixture has been allowed to settle for about 10 minutes.    Of the filtrate, 10 c.c. are neutralised with potassium hydroxide and saponified on the water-bath for 1 hour with 5 c.c. N/2 potassium hydroxide solution. In the case of pure bergamot oil, the 10 c.c. of filtrate required for saponification.

| | |
|---|---|
| 0.08 c.c. N/2 potassium hydroxide solution | = 2.2 mg. KOH |
| After adding 1 % of glyceryl triacetate. 0.58 c.c. | = 16.2 mg. KOH were used. |
| After adding 2 % of glyceryl triacetate. 1.43 c.c. | = 40.0 mg. KOH were used. |
| After adding 5 % of glyceryl triacetate. 2.79 c.c. | = 78.0 mg. KOH were used. |

Hence the addition of 1% glyceryl triacetate requires about 15 mg. KOH more for saponification.

Later, Schimmel & Co. proposed omitting the petroleum spirit and shaking 10 c.c. of the oil with 20 c.c. of 5% alcohol. After allowing the 2 layers to separate completely, 10 c.c. of the aqueous layer, which may be filtered, is neutralised, using phenolphthalein as indicator, and saponified for 1 hour with 5 c.c. of $N/2$ potassium hydroxide solution. With pure oils not more than 0.1 c.c. of $N/2$ alkali should be required, a higher figure indicating the presence of glyceryl esters. The time taken for the separation of the oil and the aqueous liquids is so long, however, that the use of petroleum spirit is preferable. For the positive identification of glyceryl acetate, the same chemists describe the following process.

40 grm. were hydrolysed with the calculated quantity of sodium hydroxide in a concentrated aqueous solution; the solution was then distilled, and, as only water passed over, it was next evaporated to dryness in a dish. The attempt to separate the alcohol (glycerol), which had been split off from the ester, from the sodium salt of the acid by means of an extracting agent failed, because the known solvents took up not only the alcohol but also considerable quantities of the sodium salt. To obviate this difficulty, the sodium salt was decomposed with the calculated quantity of dilute sulphuric acid and the organic acid which was liberated removed by distillation, and subsequently by evaporation. This acid was identified as acetic acid. It was now easy to separate the alcohol of the ester from the residual sodium sulphate by means of ethyl alcohol. When the ethyl alcohol had been evaporated by distilling *in vacuo*, the ester alcohol was identified as glycerol by its b. p. 147° (4 mm.).

As Salamon and Seaber[1] have pointed out, glyceryl acetate is so easily washed out with 5% alcohol, that an adulterated oil, when washed several times with alcohol of this strength, will show a distinctly lower ester value than the original unwashed oil. Pure oils of lavender, bergamot and similar oils show practically no reduction in ester value by such treatment.

**Non-volatile Esters.**—When non-volatile or practically non-volatile esters such as ethyl citrate are used for the purpose of adulteration, almost the whole of the esters remain in the residue left on evaporating the oil for from 3 to 4 hours on a water-bath. If the weight of this residue is above the normal for a pure oil, non-volatile esters are strongly indicated and may be approximately

[1] *Perfumery Record*, 1912, **3**, 275.

ascertained by estimating the saponification value of the residue itself. The process is carried out as follows: 5 grm. of the oil are evaporated in a platinum dish on a water-bath until the weight is practically constant. The residue is washed into a flask and saponified in the usual manner. Titration should be effected quickly with phenolphthalein as indicator. After the neutral point has been reached, the liquid will acquire a red tint in a short time. No notice need be taken of this as it is due to decomposition of bergaptene or similar substances. The saponification value of the residue from pure bergamot oil varies from about 135 to 180, usually about 170. The addition of 1% of ethyl citrate will raise it about 50, whilst the addition of 2% will raise it by nearly 100. Messrs. Schimmel & Co. have devised the following method of estimating the amount of fixed esters present as an adulterant in this type of oil. The examination of pure bergamot oil has shown that almost the whole of the acid which is combined with the potassium hydroxide on saponification can be distilled off with steam after acidifying the aqueous solution with sulphuric acid. With pure bergamot oil, therefore, only a little more potassium hydroxide solution is used in ascertaining the saponification value than is required for neutralising the acids which have been distilled off. The estimation is carried out with 1.5 to 2.0 grm. of the oil as follows: the acid and ester values are ascertained in the usual manner, and the contents of the saponification flask evaporated to dryness after adding a few drops of N/2 potassium hydroxide solution. The residue is dissolved in about 5 c.c. of water and acidified with 2 c.c. of dilute sulphuric acid. From a flask (similar to Umney's apparatus described on page 610) fitted with an ascending tube, a powerful current of steam is generated, by which, in about half an hour, 250 c.c. are distilled over into a measuring flask, in such a manner that the contents of the saponification flask are kept down to about 10 c.c. with a small flame. Afterwards 100 c.c. more are carried over in the same manner. The distillate, after a few drops of phenolphthalein solution have been added, is titrated with N/2 potassium hydroxide solution (or for the sake of accuracy, better still with N/10 solution) until it assumes a red colour. The first 250 c.c. contain very nearly the entire volatile acids, as the next 100 c.c. invariably use up only 0.1 to 0.2 c.c. of N/2 solution. From the quantity of potash solution required to neutralise the entire distillate the acid

value (II) is calculated for the weight of the bergamot oil used. The difference between the saponification value of several pure oils which have been examined and the acid value (II) estimated in the manner described above, varied (as shown in the table below, Nos. 1–7) from 5.2 to 6.9.

Hence, unless further examination of pure oils should show a higher figure, oils with a greater difference must be regarded as suspect or adulterated.

In the case of the pure esters (Nos. 12 to 14) here examined the difference between the two values was from 596.4 to 745.8. The addition of such esters to oil of bergamot must, therefore, correspondingly increase the difference of both values of the adulterated oil (Nos. 15 to 23 of the table).

| | Acid value | Ester value | Sap. value | Acid value II of the oil | Diff. |
|---|---|---|---|---|---|
| | | of the oil | | | |
| No. 1 Bergamot oil | 1.6 | 88.7 | 90.3 | 84.3 | 6.0 |
| No. 2 Bergamot oil | 1.6 | 90.2 | 91.8 | 86.6 | 5.2 |
| No. 3 Bergamot oil | 2.0 | 101.1 | 103.1 | 97.0 | 6.1 |
| No. 4 Bergamot oil | 2.3 | 112.3 | 114.6 | 107.7 | 6.9 |
| No. 5 Bergamot oil | 2.4 | 100.0 | 102.4 | 95.7 | 6.7 |
| No. 6 Bergamot oil | 2.3 | 96.1 | 98.4 | 91.8 | 6.6 |
| No. 7 Bergamot oil | 2.1 | 98.3 | 100.4 | 95.1 | 5.3 |
| No. 8 Bergamot oil | 2.0 | 98.2 | 100.2 | 90.8 | 9.4 |
| No. 9 Bergamot oil | 2.0 | 103.9 | 105.9 | 91.8 | 14.1 |
| No. 10 Bergamot oil | 2.0 | 102.4 | 104.4 | 87.6 | 16.8 |
| No. 11 Bergamot oil | 2.8 | 103.9 | 106.7 | 89.9 | 16.8 |
| No. 12 Diethyl succinate | | | 638.4 | 7.3 | 631.1 |
| No. 13 Triethyl citrate | 0.8 | 602.6 | 603.4 | 7.0 | 596.4 |
| No. 14 Diethyl oxalate | | | 753.0 | 7.2 | 745.8 |
| Bergamot oil after adding: | | | | | |
| No. 15 1 % Diethyl succinate | 2.1 | 103.5 | 105.6 | 94.1 | 11.5 |
| No. 16 2 % Diethyl succinate | 2.1 | 109.9 | 112.0 | 93.1 | 18.9 |
| No. 17 3 % Diethyl succinate | 2.1 | 116.2 | 118.3 | 92.8 | 25.5 |
| No. 18 4 % Diethyl succinate | 2.1 | 121.7 | 123.8 | 91.8 | 32.0 |
| No. 19 5 % Diethyl succinate | 2.1 | 127.6 | 129.7 | 91.5 | 38.2 |
| No. 20 1 % Triethyl citrate | 2.1 | 103.4 | 105.5 | 94.1 | 11.4 |
| No. 21 2 % Triethyl citrate | 2.1 | 109.1 | 111.2 | 92.8 | 18.4 |
| No. 22 1 % Diethyl oxalate | | | 106.6 | 94.7 | 11.9 |
| No. 23 2 % Diethyl oxalate | | | 113.3 | 92.5 | 20.8 |
| No. 24 2 % Glyceryl triacetate | 2.1 | 111.2 | 113.3 | 108.7 | 4.6 |
| No. 25 4 % Terpinyl acetate | 2.4 | 103.2 | 105.6 | 100.0 | 5.6 |

Nos. 24 and 25 show that adulteration with the esters of the volatile group cannot be detected by distilling the acids, because in these cases the difference lies of course within the limits for pure oils. The following are average figures for a number of artificial esters.

| Ester | Sp. gr. 15° C. | Ref. index 20° C. | Ester, % | Range of b. p. |
|---|---|---|---|---|
| Ethyl formate, pure................. | 0.908 | 1.3621 | 74.9 | 54°– 65° |
| Ethyl formate, commercial.......... | 0.869–0.927 | 1.360–1.367 | 59.6– 68.9 | 55°– 80° |
| Ethyl acetate, pure................. | 0.904 | 1.3740 | 100.8 | 75°– 79° |
| Ethyl acetate, commercial........... | 0.901–0.904 | 1.3737–1.374 | 82.8– 94.7 | 71°– 84° |
| Ethyl butyrate, pure................ | 0.883 | 1.3922 | 100.1 | 110°–120° |
| Ethyl butyrate, commercial.......... | 0.883–0.886 | 1.388–1.492 | 95.4–100.5 | 105°–140° |
| Ethyl succinate.................... | 1.042–1.054 | 1.419–1.421 | 98.0– 99.5 | 210°–214° |
| Ethyl sebacate..................... | 0.959–0.966 | 1.436–1.439 | 94.9– 96.4 | above 300° |
| Ethyl benzoate..................... | 1.048–1.053 | 1.504–1.545 | 73.8–100.5 | 210°–215° |
| Ethyl cinnamate................... | 1.052–1.056 | 1.557–1.559 | 99.1–100.6 | 260°–267° |
| Ethyl salicylate.................... | 1.132–1.134 | 1.521–1.523 | 96.0– 99.8 | 225°–230° |
| Amyl acetate, pure................. | 0.860–0.863 | 1.397–1.402 | 89.6– 99.6 | 130°–140° |
| Amyl acetate, commercial........... | 0.863–0.870 | 1.399–1.402 | 82.2– 88.9 | 110°– 142° |
| Amyl butyrate, pure................ | 0.867 | 1.4128 | 99.9 | 170°–180° |
| Amyl butyrate, commercial.......... | 0.857–0.867 | 1.407–1.412 | 76.9– 83.4 | 135°–180° |
| Amyl valerate, pure................ | 0.858 | 1.4131 | 98.7 | 180°–190° |
| Amyl valerate, commercial.......... | 0.850–0.866 | 1.408–1.413 | 75.6– 81.8 | 140°–190° |
| Amyl salicylate.................... | 1.048–1.053 | 1.505–1.508 | 97.2– 98.7 | 260°–275° |

Umney (*P. E. O. R.*, 1914, **116**) has published a critical study of the above method, and recommends the use of the following apparatus in making the estimation:

1. A 3 litre Jena glass flask.

2. A rubber connection by which the steam can be immediately cut off.

3. A long necked $CO_2$ flask, of Jena glass, of 150 c.c. capacity.

4. A splash head to fit into the $CO_2$ flask.

5. A Davies condenser.

6. A 500 c.c. Erlenmeyer flask.

The results obtained, unless special precautions are adopted, are usually too high. Some causes of error are the following:

1. The use of methylated spirit (unless purified by redistillation) in the saponification.

2. The use of hydrochloric acid in neutralising excess of alkali in the saponification.

3. Failure to boil the water to drive off $CO_2$ before connecting up the steam supply.

4. The use of sulphuric acid to acidulate before distillation, as this acid is sometimes reduced to sulphurous acid in the process. Phosphoric acid is recommended instead of sulphuric acid.

Reclaire (*P. E. O. R.*, 1923 **293**) has carried out a series of experiments in reference to the process advocated by Schimmel & Co. for the detection of esters of fixed acids, which, with its modification suggested by J. C. Umney, has been described above.

He finds that it is unnecessary to evaporate the saponification liquor to dryness before distilling off the volatile acids, and gives the following series of analyses to indicate the effect of the use of sulphuric, phosphoric and tartaric acids.

The oils in question were lavender, bergamot, petitgrain and geranium oils adulterated with ethyl phthalate, succinate, tartrate and citrate.

| | Sap. value of oil | Evaporating and using ·sulphuric acid | Not evaporating: sulphuric acid | Evaporating: phosphoric acid | Not evaporating: phosphoric acid | Not evaporating: tartaric acid |
|---|---|---|---|---|---|---|
| 1 | 126.9 | 103.6 | 103.6 | 103.6 | 104 | 103.6 |
| 2 | 182.9 | 94.2 | 92.4 | 92.4 | 92.1 | 92.4 |
| 3 | 128.8 | 101.7 | 98.5 | 99.8 | 98.5 | 103.2 |
| 4 | 157.8 | 139.1 | 138.1 | 138.1 | 138.6 | 140.9 |
| 5 | 160.5 | 138.1 | 138.1 | 138.1 | 138.1 | ............ |
| 6 | 149.3 | 124.1 | 123.2 | 125.6 | 125.6 | 121.3 |
| 7 | 149.3 | 121.3 | 123.2 | 120.4 | 122.2 | 123.8 |
| 8 | 80.6 | 74.7 | 66.2 | 70.5 | 69.6 | 69 |

Bennett and Garratt (*P. E. O. R.*, 1923, **359**) state that with some cases of pure lavender oil, the omission to evaporate causes misleading results, and they also do not agree with Schimmel & Co. that the first 250 c.c. of the distillate contains nearly all the volatile acids. In the case of some pure lavender oils as much as 450 c.c. must be distilled. They propose the following simple method, which, they claim, will detect 1% of any of the following esters, namely: citrates, tartrates, succinates, benzoates, phthalates and cinnamates.

The test depends upon the insolubility in absolute alcohol of the potassium salts of certain organic acids. One c.c. of the oil under examination is placed with 3 c.c. of an approximately 10% solution of potassium hydroxide is absolute alcohol in a test tube, the whole immersed in a water bath for a few minutes and then allowed to cool. If no precipitate forms within at most one hour the oil may be considered unadulterated with these esters.

*Phthalate.* A crystalline precipitate forms almost at once with as little as 1%.

*Cinnamate.* With 2.5% precipitate forms quickly; with 1% crystals are deposited after some time.

*Succinate.* With 2.5% a gelatinous mass is produced; with 1% a crystalline precipitate is formed.

*Citrate and Tartrate.* A heavy cloudiness is produced, and a crystalline deposit on standing.

*Benzoate.* With 2.5 % a crystalline deposit appears after standing for some time.

According to Béhal (*Bull. Soc. Chim.*, 1914, 306) the results of the estimation of esters may show differences of between 1 and 3 %, especially when formic or acetic esters are in question. He attempts to explain these differences by the suggestion that when esters of high molecular weight are saponified with alcoholic potash, esters of lower molecular weight are first formed, principally ethyl formate and ethyl acetate. Being highly volatile, these are liable to be lost through incomplete saponification. But so long as an efficient condenser is employed this loss does not occur.

In examining an essential oil for artificial esters, it is always worth while shaking the oil with warm water and observing the difference, if any in the refractive indices. In the presence of glyceryl acetate a distinct alteration in the refractive index is to be noted, owing to the ester being washed out by the water.

Again, if, for example, bergamot oil is evaporated on the water bath and the last 10 % be examined, the natural oil leaves a residue whose refractive index is at least 1.509, a figure which is reduced by most artificial esters.

When the saponification liquor is examined for foreign acids which may have been present in the form of esters, the following reactions should be noted:

|  | $BaCl_2$ | $CaCl_2$ | $F_2Cl_6$ |
|---|---|---|---|
| Benzoate............. | no ppt. | no ppt. | buff ppt. |
| Butyrate............. | no ppt. | no ppt. | no ppt. |
| Cinnamate........... | white ppt. | white ppt. | buff ppt. |
| Citrate.............. | white ppt. | white ppt. on boiling | green colour |
| Formate............. | no ppt. | no ppt. | red colour |
| Oleate............... | white ppt. | white ppt. | brown ppt. |
| Phthalate............ | no ppt. | no ppt. | brown ppt. |
| Oxalate.............. | white ppt. | white ppt. | green ppt. |
| Succinate............ | no ppt. | no ppt. | brown ppt. |
| Tartrate............. | white ppt. | ............ | green colour with brown ppt. on heating |

Hall and Harvey (*P. E. O. R.*, 1913, 6) prefer to estimate glyceryl acetate by weighing the separated glycerol. About 8 to 10 grm. of the oil is mixed with 50 c.c. of 95 % alcohol and saponified with seminormal alcoholic potash. The mixture is then digested on the water bath for an hour, neutralised with seminormal hydrochloric

acid and evaporated to dryness on the water bath to remove the alcohol. About 20 c.c. of water is now added and the oil extracted by means of ether, and the aqueous liquids eparated into a round bottomed flask. The ether extract is washed with 10 c.c. more water which is added to the water in the flask, and the whole evaporated to a syrupy condition. The glycerin present in this aqueous liquid is then estimated in the usual manner.

Phthalic acid can be detected in the saponification liquor by extraction with ether after acidification, and heating the residue with resorcinol and a few drops of sulphuric acid when the characteristic phthalein fluorescence results.

*The Estimation of Esters in Flavouring Essences.*—A great majority of the flavouring essences of commerce are either entirely artificial, or are mixtures of a little natural fruit essence with a considerable amount of artificial esters and other substances. The following method, which is the official method of the United States Bureau of Internal Revenue yields approximately accurate results in the estimation of esters in such mixtures.

Introduce 10 c.c. of 50% (by volume) alcohol into a 500 c.c. Erlenmeyer flask and add 10 c.c. of the essence (or half that quantity when the essence contains as much as 5% of esters calculated as ethyl acetate). The flask is then connected with an upright condenser, the end of which is fitted with a rubber stopper with a mercury valve. A 100 c.c. Kohlrausch flask is fitted to the rubber stopper and the solution is distilled until 100 c.c. are collected, the rate of distillation being very slow. The distillate is transferred to a 500 c.c. Erlenmeyer flask, the last portion beng rinsed out with a few drops of 50% alcohol. A few drops of phenolphthalein solution are added and the liquid neutralised. N/10 caustic soda is then added in quantity to amount to about 25% above that nesessary for complete saponification. The flask is stoppered and allowed to stand overnight and then boiled under a reflux condenser for half an hour. A blank experiment should be conducted simultaneously, and the necessary correction made. The esters are calculated to ethyl acetat?.

## Estimation of Aldehydes and Ketones

Certain essential oils, as, for instance, the oils of bitter almonds, cassia, cinnamon, citronella, and lemon-grass, are chiefly composed

of aldehydes. These may be detected by most of the general tests for aldehydes and may generally conveniently be estimated by converting them into their bisulphite compounds.

The method usually adopted for the estimation of aldehydes and ketones which form bisulphite compounds is some variation of the original absorption process with a hot saturated solution of sodium hydrogen sulphite. It must be remembered that all absorption processes are merely approximate owing to the slight solubility of the constituents which are called non-absorbable, and the incomplete absorption which may happen with the absorbable compounds.

Oils such as cassia and lemon-grass are those upon which this estimation is most frequently necessary. The estimation of citral in lemon oil is attended with many difficulties, and has been dealt with under "Citral."

The condition requisite for an accurate estimation is that the non-absorbable layer of oil should separate sharply from the absorption liquid without any waxy or fluocculent substances to interfere with a correct reading.

The absorption is carried out in a Hirschsohn flask, a flask holding about 150–200 c.c., and having a long neck graduated to 10 c.c. in 0.1 c.c. 5 or 10 c.c. of the oil are introduced into the flask, and a hot 30–40% solution of sodium hydrogen sulphite added to about $\frac{1}{3}$ of the capacity of the flask. In the case of cassia oil, the absorption is facilitated by standing the flask with the oil in it in the water-bath for 5 minutes before adding the solution. The whole is well shaken, care being taken that none of the crystals formed get into the neck of the flask, as they often remain firmly attached there and render the absorption very tedious. The flask is now placed in boiling water, and shaken from time to time with the addition of more bisulphite solution. This is continued until the whole of the crystals are absorbed, and nothing but a clear oily layer floats on the surface. More solution is carefully run in, until the oily layer is forced up into the neck. The flask is allowed to stand for 4 hours at least and then the non-absorbed layer is read off, the difference being taken as aldehyde or ketone. The separation of the non-absorbable layer by means of ether, with subsequent removal of the ether and weighing the oil has been suggested, but this method has no advantage over the other, and is far more tedious. Burgess (*Analyst*, 1904, **29,** 78) has examined the various processes for the estimation of

aldehydes and ketones, and his results may be summarised as follows (see also under Citral):

1. By the use of sodium hydrogen sulphite (as just described). He objects to the time required, and the frequent separation of resinous matter which renders the reading of the meniscus at the point of separation difficult. This is, however, as pointed out above, only true in certain cases.

2. By condensation with cyanacetic acid in the presence of potassium hydroxide. He considers that absorption with this reagent always gives too high results. The reagent was first suggested by Tiemann, and afterward recommended by E. J. Parry, who, however, has since shown that an absolutely fresh specimen of cyanacetic acid is necessary to obtain results which approximate to the truth. In practice this method is rarely used.

3. Absorbing the oil by a saturated solution of sodium salicylate. It is clear that sodium salicylate forms compounds with many oxygenated compounds in essential oils, but probably substances other than aldehydes and ketones are absorbed, and the method has been discarded.

4. The hydroxylamine method. This method depends on the fact that many aldehydes and ketones form oximes when acted on by excess of hydroxylamine in alcoholic solution. The amount of unused hydroxylamine is estimated by titration, and from the amount that has entered into combination, the amount of aldehyde or ketone is deduced. This method appears to have some advantages in the case of oils containing a small amount of aldehyde, but some difficulty is usually experienced in deciding upon the end-point of the titration. It is, in practice, only used for the estimation of citral in lemon oil, and has therefore been described at length under "citral." Burgess states that the conditions of this estimation vary with different oils, and that no definite instructions can be prescribed which will apply to all oils.

5. By the use of semioxamizide. Hanus has recommended the use of this substance (*Pharm. Cent.*, 1904, 37). It is only suggested for the estimation of cinnamaldehyde in cassia and cinnamon oils, and is described below.

6. By the use of a neutral solution of sodium sulphite. This is the method which Burgess prefers, and is applicable to a very large number of essential oils.

The oil (5 to 10 c.c.) is absorbed, as in the case with sodium hydrogen sulphite, in a Hirschsohn flask, with a saturated solution of neutral sodium sulphite, a soluble sulphonate being formed.   In the case of citral, for example, the following reaction takes place:

$C_9H_{15}CHO + 2Na_2SO_3 + 2H_2O = C_9H_{17}(NaSO_3)CH.OH.SO_3Na +3NaOH.$
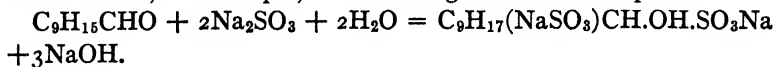
The flask containing the mixture is heated on a water-bath, 2 or 3 drops of phenolphthalein being added.   As combination proceeds, alkali is liberated and a red colour is developed.   This is discharged by the careful addition of 10% acetic acid, the mixture being so kept neutral until no further liberation of alkali is observed.   The unabsorbed oil is then forced by the addition of further sulphite solution into the neck, and after due time for all the globules of oil to separate, the oil layer is read.   By this method good results may be obtained in the case of the following oils: bitter almond, caraway, cassia, cinnamon, citral-containing oils, citronella (if heated for a very long time), cumin (litmus is the better indicator, with this oil), pennyroyal (litmus is the better indicator), spearmint.          `

In oils containing only a small amount of aldehydes, such as lemon oil, this method does not succeed, as the reading of the meniscus is obscured by the presence of some flocculent matter.

Schimmel and Co. (*Bericht*, November, 1908, 83), states that, in the case of lemon-grass oil, sodium sulphite acts only on the citral, whereas the hydrogen sulphite reacts with part, at least, of the methyl-heptenone.   Hence different results are obtained by the two processes.

A result of 2 to 5.5% higher is thus obtained by the use of the hydrogen sulphite than with the neutral sulphite process, which gives more accurate results.   At the same time the acid sulphite method is the process almost universally employed with this oil, and therefore it is necessary to state the process used in comparing results obtained.

The latest critical examination of the details necessary in carrying out the sulphite and bisulphite absorbtion processes for the estimation of aldehydes and ketones in essential oils is that of C. T. Bennett and F. C. L. Bateman (*P. E. O. R.*, 1923, **268**).   It is pointed out that in the English edition of Gildemeister's "Volatile Oils" the directions given in connection with the bisulphite method are to use 10 c.c. of the oil with an equal volume of 30% bisulphite solution, and in footnotes (on page 583) it is stated: "(1) In the case of oils that

contain less than 40 per cent. of aldehyde only 5 c.c. are taken, or a flask is used, the neck of which has a capacity of 10 c.c. and is calibrated from 1 to 10. (2) Care should be taken that the solution does not contain too much free sulphurous acid, since this retards the reaction. If necessary, the solution should be neutralised somewhat by the addition of sodium carbonate."

Bennett and Bateman do not agree with the use of 10 c.c. of the oil, and consider that 5 c.c. gives more accurate results. Nor do they consider an equal volume of bisulphite solution sufficient for the oil to be shaken with. With 5 c.c. of oil they consider 50 c.c. of the bisulphite solution should be used. As powdered bisulphite rapidly deteriorates, they recommend the use of the crystals in all cases. The shaking must be vigorous and continuous.

With regard to the neutral sulphite process, it is stated that the method of the British Pharmacopœia gives too low results and that 5 c.c. of the oil should be shaken with 50 c.c. of a 30 per cent. solution of sodium sulphite followed by successive quantities of sodium sulphite solution until the reaction is complete. The following ⸱results were obtained with mixtures of 100 per cent. cinnamic aldehyde with copaiba oil.

|  | WITH | |
| --- | --- | --- |
|  | 5 C.C. OF OIL | 10 C.C. OF OIL |
| Cinnamic aldehyde 40% | | |
| with 100 c.c. of 20% sulphite of sodium.......... | 43% | 41% |
| with 70 c.c. of 20% sulphite of sodium.......... | 40% | 37% |
| with 75 c.c. of 30% bisulphite of sodium....... | 40% | 38% |
| with 75 c.c. of 30% potassium bisulphite........ | 40% | 40% |
| Cinnamic aldehyde 60% | | |
| with 100 c.c. of 20% sulphite of sodium.......... | 62% | 58% |
| with 70 c.c. of 20% sulphite of sodium.......... | 60% | 52% |
| with 75 c.c. of 30% bisulphite of sodium....... | 58% | 58% |
| with 75 c.c. of 30% potassium bisulphite......... | 60% | 58% |
| Cinnamic aldehyde 70% | | |
| with 100 c.c. of 20% sulphite of sodium.......... | 68% | 63% |
| with 70 c.c. of 20% sulphite of sodium. ........ | 68% | 56% |
| with 75 c.c. of 30% bisulphite of sodium........ | 68% | 67% |
| with 75 c.c. of 30% potassium bisulphite........ | 69% | 70% |
| Cinnamic aldehyde 40% | | |
| with 70 c.c. of 30% sulphite of sodium........... | 40% | 39% |
| Cinnamic aldehyde 60% | | |
| with 70 c.c. of 30% sulphite of sodium........... | 60% | 57% |
| Cinnamic aldehyde 70% ⸱ | | |
| with 70 c.c. of 30% sulphite of sodium........... | 70% | 65% |

The method recommended by Hanus (*Pharm. Central.* (1869), **37, 1094**) is as follows. It is restricted to the estimation of **cinnamic aldehyde.** 10 grm. of finely powdered hydrazine sulphate are dissolved in a solution of 9 grm. of sodium hydroxide in 100 c.c. of water, and the

alkali sulphate produced is precipitated by the addition of 100 c.c. of alcohol.    After filtering, the solution is warmed, 9 grm. of oxamethane are added in small portions, the whole warmed for half an hour and allowed to cool.    The azide separates in crystalline tables, and these are separated and recrystallised.    To estimate the aldehyde by means of this reagent, a small quantity, not more than 0.2 grm., of the oil is well shaken in 85 c.c. of water, and about 0.35 grm. of semioxamazide in 15 c.c. of hot water is added, and the whole well shaken.    After 5 or 10 minutes the compound begins to be precipitated, and after standing 24 hours can be collected on a Gooch filter washed with cold water and dried for a few minutes at 105°.    The amount of the precipitate is multiplied by 0.6083 to obtain the amount of aldehyde.    The constitution of the semi-oxamazone of cinnamic aldehyde is $NH_2.CO.CO.NH.N:CH.CH:CH.-C_6H_5$.

Feinberg has obtained good results in estimating aldehydes as $p$-nitrophenylhydrazone by the method of W. Alberda van Ekenstein and J. J. Blanksma (*Chem. Zentralbl.*, 1905, **1**, 1277).    In the case of benzaldehyde he proceeds as follows: 25 c.c. of a 1% benzaldehyde solution (in 12% acetic acid, are diluted with 50 c.c. of water and mixed with 30 c.c. of 30% acetic acid containing double the calculated quantity of $p$-nitrophenylhydrazine.    After 5 hours the precipitate is collected in a Gooch crucible and washed with 10% acetic acid until a well defined coloration has ceased to ensue upon the addition of alkali.    The precipitate is then dried at 105° to 110° and weighed.    The benzaldehyde-content is found by multiplying by 0.44.    It is necessary to ascertain by titration the quantity of benzoic acid which is present in the benzaldehyde, and to deduct it from the quantity of benzaldehyde used.    The average proportion of benzaldehyde found was about 99%.    The same method applies to salicylic aldehyde, but in this case filtration may be commenced after 1 hour (factor 0.4747).

For **vanillin** and **anisic aldehyde** Feinberg gives the following method: Dissolve 0.5 grm. of aldehyde in a little alcohol and acetic acid, and after diluting with 75 c.c. of water and warming, mix the solution, drop by drop, with constant stirring, with a solution of $p$-nitrophenylhydrazine in $2N$-hydrochloric acid.    Filter after 30 minutes in a Gooch crucible and wash with $2N$-hydrochloric acid and afterwards with water until only a faint opalescence is pro-

duced by silver nitrate.    For the estimation of the anisic aldehyde use the factor 0.50188; for vanillin, 0.5353.

Bruylants (*Bull. Acad., R. Belg.*, 1907, **11**, 955) has published a method for the estimation of aldehydes, especially as applied to oil of lemon.

It is based on the fact that after adding ammonium sulphide to defibrinated blood in the presence of a small quantity of aldehyde, the two absorption lines of oxyhæmoglobin diminish in intensity until a third line appears between them, which becomes more and more distinct, and finally becomes as intense as the other lines.    The following instruments and reagents are required to carry out the method: a spectrophotometer, the field of view of which, for the purpose of comparative observations, is divided into 2 superincumbent equal parts, and the necessary vessels for holding the solutions, burettes, and test-tubes; a 3% blood-solution prepared from fresh defibrinated pig's blood which in the spectroscope shows the two characteristic lines of oxyhæmoglobin; a solution of ammonium sulphide, which must be prepared with particular care in order to obtain the desired effect (a definite volume of ammonia is saturated with hydrogen sulphide gas, mixed with a slightly larger volume of ammonia, and the ammoniacal sulphide thus obtained exposed to the light for a few days); citral solutions with 3, 4, and 5% citral in citral-free oil (for comparison), and finally 94% alcohol, freed from aldehyde by boiling with potassium hydroxide and metaphenylene-diamine hydrochloride.

Before the estimation is carried out, preliminary tests must be made so as to obtain an approximate aldehyde content.    Samples of 9 c.c. of the blood solution are mixed under exactly the same conditions with 1 c.c. ammonium sulphide solution each, and then, without shaking, the solution of the oil under examination, or the 5% comparison citral solution at the same time slowly poured on the top.    Both solutions are prepared in the proportion of 5 c.c. alcohol to 1 c.c. of the aldehyde-containing oil.    First of all 0.15 c.c. of such solution are added.    Next, the vessels are shaken for about half a minute.    After separating the insoluble portions, the lower layer is removed by means of a pipette, and placed in the vessel of the spectroscope.    If the work is done sufficiently quickly, it is possible to determine first of all the absorption lines of oxyhæmoglobin in both parts of the field of view; next the line in the middle appears as

the first phase of the reaction, and it does so in both parts simultaneously if the aldehyde quantities in the two solutions are absolutely equal. If this is not the case, the quantity of the alcoholic solution of the oil is increased or diminished by hundredth parts of a c.c., while the quantity of the test-solution remains unchanged. After 5 or 6 tests the aldehyde content can thus be approximately estimated. In the exact estimation which now follows, the work is carried on with a comparative solution of which the aldehyde content approaches as closely as possible that of the oil under examination. If the oil contains less than 5% of aldehydes, a commencement should be made with a comparison solution containing 3 or 4% of citral—if more than 5% of aldehyde, the 5% solution is employed, and the work is discontinued, exactly as before, when the central absorption lines appear simultaneously. After some practice, a complete estimation can easily be carried out in half an hour. The results are very exact.

The following methods are mainly of theoretical interest, and are rarely employed except in research work.

**Aldehydes and ketones** may also be isolated by converting them into the corresponding *semicarbazones* by reaction with semicarbazide.[1]

A solution of semicarbazide is conveniently prepared in accordance with the directions of Thiele and Stange (*Annalen*, 1894, **281**, 19) by dissolving together 130 parts of hydrazine sulphate, 55 of sodium carbonate, and 85 of sodium cyanate in 1000 parts of water. 100 c.c. of this solution is treated with 150 c.c. of alcohol, and the liquid filtered after standing for several hours. A weight of 10 grm. of the aldehyde to be tested is then added to the clear filtrate. The semicarbazone crystallises out gradually and the greater part separates in the course of 24 hours. The liquid is then filtered and the semicarbazone still in solution precipitated by addition of water and recrystallised from alcohol. The united products are then purified by solution in methyl alcohol and precipitation by water.

## Carbonyl Number

Benedikt and Strache (*Monatsh.*, 1893, **14**, 270) have proposed to estimate the total amount of *ketones* and *aldehydes* present in an

[1] *Semicarbazide*, or carbamic hydrazide, $NH_2.CO.NH.NH_2$, may be prepared by heating a mixture of molecular proportions of urea and hydrazine hydrate for 3 hours in a sealed tube at 100°. It crystallises in colourless prisms melting at 96°, and reduces Fehling's solution and ammoniacal silver nitrate in the cold. When shaken with aldehydes, semicarbazide yields characteristic crystalline compounds (semicarbazones).

essential oil by ascertaining the carbonyl number or yield of *hydrazone* obtained by treating an alcoholic solution of the sample with phenyl-hydrazine hydrochloride and sodium acetate, used in quantity roughly proportionate to the aldehydic and ketonic substances present. If the carbonyl number is above 40, from 0.5 to 1.2 grm. of the substance is treated with a weight of phenyl-hydrazine hydrochloride between 1 and 1.5 times the weight of the oil. With a carbonyl number between 10 and 40, from 1 to 2 grm. of substance should be employed with from 0.5 to 1 grm. of the reagent. When the carbonyl number is below 10, from 2 to 5 grm. of the sample and 0.5 grm. of the reagent should be used. In any case a quantity of sodium acetate is added equal to 1.5 times the weight of phenylhydrazine hydrochloride employed, and preferably in 10% alcoholic solution. The mixture is warmed on the water-bath for a quarter of an hour in a flask holding about 100 c.c., and filled about two-thirds with the alcoholic fluid, whereby too vigorous ebullition is avoided; after cooling, the liquid is diluted to 100 c.c. with water, the insoluble matter filtered off through a dry filter, and 50 c.c. of the filtrate oxidised with Fehling's solution. The nitrogen thereby evolved is collected and measured, so as to ascertain the amount of unaltered phenylhydrazine in the liquid, and thus obtain the data for estimating the quantity precipitated as hydrozone. For this purpose a stand-



Fig. 9.

ard solution of phenylhydrazine may be conveniently used in the first instance, containing about 5%, its precise strength being estimated by treating a known volume with Fehling's solution. The salt must be free from aniline. The purification of the nitrogen from benzene vapour is necessary when accurate results are desired, and is effected by Benedikt and Strache by the arrangement shown in Fig. 9. The longer end of the U-tube is fixed to a stoppered reservoir, the shorter end being drawn out to a fine point and placed inside the tube containing the nitrogen to be purified. About 200 c.c. of alcohol is now allowed to run down from the reservoir so as to spurt upward in a fine jet into the nitrogen tube; this absorbs
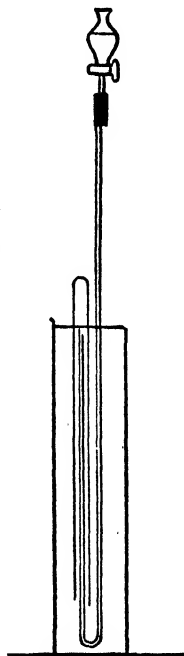
all benzene vapour present in the nitrogen. In turn, some 400 c.c. of water is similarly passed down from the reservoir to absorb alcohol vapour, after which the measuring tube is removed to another vessel containing water, and the volume of the nitrogen read off. A number of direct observations with nitrogen, to which benzene was added after measurement, showed that this method of treatment sufficed to remove all benzene vapour within the limits of reading-error.

A Lunge's nitrometer can be conveniently substituted for the above arrangement.

Duplicate estimations made in this way are stated rarely to differ more than at most 1 or 2 units in the value of the carbonyl number deduced, but this value sometimes exhibits a considerable divergence from the actual amount of aldehyde or ketone present. The following figures were obtained with different samples of oils containing large proportions of aldehydic or ketonic constituents:

| Oil, etc. | Carbonyl number | Aldehyde or ketone present | % of aldehyde or ketone |
|---|---|---|---|
| Cumin.................. | 51.8 | Cuminal, $C_{10}H_{12}O$.......... | 47.9 |
| Cumin.................. | 45.2 | Cuminal, $C_{10}H_{12}O$.......... | 41.8 |
| Cumin.................. | 96.7 | Cuminal, $C_{10}H_{12}O$.......... | 89.4 |
| Caraway............... | 42.0 | Carvone, $C_{10}H_{14}O$.......... | 39.3 |
| Caraway............... | 33.6 | Carvone, $C_{10}H_{14}O$.......... | 31.5 |
| Caraway............... | 38.3 | Carvone, $C_{10}H_{14}O$.......... | 35.9 |
| Caraway............... | 61.1 | Carvone, $C_{10}H_{14}O$.......... | 57.3 |
| "Carvol"............... | 84.0 | Carvone, $C_{10}H_{14}O$.......... | 78.8 |
| Bitter-almond.......... | 147.5 | Benzaldehyde, $C_7H_6O$....... | 97.7 |
| Bitter-almond, free from hydrocyanic acid...... | 147.7 | Benzaldehyde, $C_7H_6O$....... | 97.7 |
| Bitter-almond, artificial.. | 145.3 | Benzaldehyde, $C_7H_6O$....... | 96.2 |
| Cinnamon.............. | 92.7 | Cinnamic aldehyde, $C_9H_8O$.. | 76.5 |
| Cinnamon.............. | 77.4 | Cinnamic aldehyde, $C_9H_8O$.. | 63.9 |
| Cassia................. | 94.3 | Cinnamic aldehyde, $C_9H_8O$.. | 77.8 |
| Cassia................. | 79.9 | Cinnamic aldehyde, $C_9H_8O$.. | 66.0 |

For the preparation of the condensation products of aldehydes (e.g., geranial) with acetone, in such a manner as to avoid secondary reactions, W. Stiehl recommends the following mode of operating:

A weight of 50 grm. of the well-dried and freshly distilled aldehyde is dissolved in 50 c.c. of absolutely dry acetone, and the solution cooled down to 0° at least. A weight of 2.5 grm. of sodium is dis-

solved in 50 c.c. of strictly absolute alcohol, and the solution also cooled down to 0°. Finally, 10 grm. of tartaric acid are dissolved in 50 c.c. of water. The solution of sodium ethoxide is then added to the solution of the aldehyde in acetone, the mixture being kept cool and continually stirred, and in 15 minutes the action is interrupted by the addition of the solution of tartaric acid. The acetone and alcohol are then distilled off in a current of steam, and the residual oil is separated from the solution of tartaric acid and washed. The oil thus obtained is distilled with superheated steam and then recti- fied, either under diminished pressure, or purified by means of a solution of sodium hydrogen sulphite. For this purpose a 50 grm. portion of the crude acetone condensation product is boiled with 100 c.c. of commercial solution of sodium bisulphite and 100 c.c. of water for about 3 hours under a reflux condenser. After the whole is cooled down the small quantities of substances which are not ketones are carefully removed by agitation with ether, and the sulphite compound decomposed in the cold with sodium hydroxide. The separated oil is well washed, and rectified, first with superheated steam and then under diminished pressure.

O. Doebner (*Ber.*, 1894, **27,** 252 and 2020) has described a reaction which appears to be strictly characteristic of the *aldehydes*, and does not take place with other compounds containing a CO— group, such as ketones, lactones, and dibasic acids.[1] The test is applied by treating the aldehyde with molecular proportions of pyroracemic acid (pyruvic acid) and $\beta$-naphthylamine, when a crystalline compound is formed having the constitution of an $\alpha$-alkyl-$\beta$- naphthocinchoninic acid. The reaction is applied by Doebner to the detection of citral and citronellal (see pages 516 and 517).

## The Iodine Value of Essential Oils

The only reason that this process has been applied to essential oils is because the word "oils" is common to them and to the group of substances classed as fatty oils. These latter are all in close chemical relationship, and the various members are very constant in character. For a process to be applicable to a group of compounds, it is obvious that the reactions taking place in that process should be the same, or

---

[1] Doebner's reaction occurs in every case tried except that of hydroxyaldehydes, such as glycerose, in which a hydroxyl-group is linked to the carbon atom to which the aldehydic residue is attached. Doebner considers this an explanation of the fact that sugars which are regarded as having an aldehydic constitution do not respond to the test.

nearly the same in all the members of that class of compounds.    This is true in the case of the fatty oils, where one has simply to consider the amount of addition—with in some cases some substitution—of iodine to, or in, the molecule of fatty acid.    In fact, the iodine process is to be regarded as a measure of the amount of unsaturated fatty acids.    To apply it to essential oils is to distort its purposes and value almost to an absurd point.    The papers of Barenthein, Davis, Snow, Williams, and Cripps on this subject need only to be examined together to cause the process to be left severely alone as applied to essential oils.    These substances, in the first place, consist of such widely different classes of substances, that the reactions taking place are different in almost every group.    Hence the iodine value ceases to have the precise meaning that it has in the case of fatty oils.    Secondly, with many of the substances found in essential oils, the reactions are so energetic that it is impossible to control them quantitatively.    Thirdly, the reactions are such that the slightest variation in temperature, exposure to light, time of reaction, and—which is most important—the excess of iodine used over that which can possibly enter into action, so influence the result that the same worker can but rarely obtain concordant values with the same sample.

It is true that there are cases where these conditions are not accentuated and where fairly constant results can be obtained.    These are, however, but few, and the process is not worth serious consideration in regard to this group of substances.    A few examples of the unreliability of the iodine value may here be given.

Aniseed oil is one which varies but little, and its composition is such that, if there were any theoretical quantitative reaction possible by this process, it would be very constant.    The values recorded by Barenthein, Davis, and Shaw, respectively, are 164, 190, and 121. Clove oil is one which contains usually between 80 and 90% of eugenol, the remainder consisting mainly of one or more sesquiterpenes.    In spite of this not very wide variation in composition, the same 3 observers give 270, 349–367, and 467.

Again, Williams, on 2 samples of aniseed oil, found 274 and 186, a difference that can never be shown to have any ratio to the difference in composition.    In practice to-day no chemist used to examining essential oils employs this very unreliable process, except in very rare cases, such as the high-boiling fractions of turpentine oil.

## Methoxyl Values of Essential Oils

The estimation of the proportion of methyl or equivalent alkyl radical eliminated from the molecule by treatment with hydriodic acid, was proposed by S. Zeisel in 1886 as a method of differentiating essential oils. The process consists in heating the compound with concentrated hydriodic acid, and receiving the alkyl iodide formed in an alcoholic solution of silver nitrate. From the weight of silver iodide produced that of the alkyl radical (in terms of methyl or methoxyl) can be calculated, since AgI corresponds to $CH_3O$. Zeisel's method has been somewhat modified by Benedikt and Grüssner (*Chem. Zeit.*, 1889, **13**, 872) who operate as follows: From 0.2 to 0.3 grm. of the substance is placed in a flask of 30 to 35 c.c. capacity, and treated with 10 c.c. of hydriodic acid of 1.70 sp. gr.[1] The flask is heated in a bath of glycerin, a current of carbon dioxide being passed through it.[2] The alkyl iodide formed passes through a series of bulbs, the first of which is empty, the second contains water, while the third contains water holding purified red phosphorus in suspension.[3] The bulbs are surrounded with water, the temperature of which can be kept, if desired, at 70.° (which is necessary in the estimation of ethoxyl, $C_2H_5O$). After passing the bulbs, the alkyl iodide, which is quite free from hydriodic acid and iodine, is absorbed in a flask containing 5 c.c. of a 40% aqueous solution of silver nitrate and 50 c.c. of 95% alcohol. As a precaution, the gas is further passed through a mixture of 1 c.c. of the silver solution with 10 c.c. of alcohol. The mixed silver solutions are diluted with water, acidified with nitric acid, and the silver iodide filtered off and weighed.[4] By multiplying the weight found by the factor 0.132 ( $= \frac{31}{235}$ ), the equivalent of methoxyl ($CH_3O$) may be found.

[1] Herzig makes an addition of 8 % of acetic acid to the hydriodic acid (*Monatsh.*, 1888, **9**, 544). The hydriodic acid employed should be free from sulphur and phosphorus compounds and should be tested by means of a blank experiment.

[2] W. H. Perkin (*Trans.*, 1903, **83**, 1367) employs a special form of long-necked distilling flask designed to prevent hydriodic acid from distilling over with the alkyl iodide, the latter being absorbed by impinging on the surface of the liquid in the first flask and by bubbling the gases through the liquid in the second flask.

[3] G. Gregor replaces the red phosphorus and water in the third bulb by a solution of 1 part of arsenious oxide and 1 of potassium carbonate in 10 parts of water. According to W. Kropatschek, the solution of these substances should not be stronger than 1 and 2 %. The bulb is liable to become choked with the precipitated arsenious oxide unless refilled for each determination. Not the slightest reduction of the silver nitrate solution in the flask takes place, as in the case when the bulb contains phosphorus.

[4] In the presence of sulphur compounds, a black precipitate is formed in the silver solution, and it is necessary to estimate the actual weight of iodine precipitated, instead of merely weighing the precipitate. Or the precipitate may be treated with dilute nitric acid till the silver sulphide is dissolved. A modified process for the estimation of the methoxyl group in compounds containing sulphur has been proposed by F. Kaufler, *Analyst*, 1902, 126.

Instead of weighing the silver iodide, G. Gregor (*J. Soc. Chem. Ind.*, 1898, **7**, 609) absorbs the alkyl iodide in a solution of silver nitrate of known strength, and subsequently ascertains the excess of silver in the filtered liquid.

The above methods are evidently inapplicable in the presence of alcohol, but may, on the other hand, be employed for the estimation of alcohol when the true methoxyl value of the oil is known. Absolute alcohol has the methoxyl value 674 $\left(\dfrac{31 \times 1000}{46} = 674\right)$.

Herzig and Meyer have proposed to differentiate between the methyl radical when attached to oxygen (methoxyl), and when attached to nitrogen (methylimine). They find that, by a suitable modification of Zeisel's process, boiling hydriodic acid liberates the methyl radical from methoxyl only, while a temperature of 200° to 300° is required for the hydrolysis of the methylimine radical. M. Busch, however (*Ber.*, 1902, **35**, 1565), states that the decomposition of the methylimine radical occasionally occurs when the compound containing it is simply boiled with hydriodic acid. Thus, if a negative result be obtained with any compound when boiled with hydriodic acid, the absence of methoxyl may be regarded as proved, but a positive result should not be accepted as conclusive evidence of its presence.

In the case of oils containing esters of higher alkyl radicals, such as butyl, amyl, and hexyl, the liquid above the silver precipitate does not become clear even if the treatment with hydriodic acid be continued for many hours, since small quantities of alkyl iodides are continually passing over.

| Name of oil | Origin | Methoxyl value | Name of oil | Origin | Methoxyl value |
|---|---|---|---|---|---|
| Anise.......... | Schimmel & Co. | 171.1 | Cinnamon-leaf... | ................ | 151.3 |
| Birchwood tar.. | ................ | 46.3 | Elemi........... | Schimmel & Co. | 25.0 |
| Cumin......... | ................ | 17.2 | Gaultheria....... | Artificial winter-green oil. Schimmel & Co. | 184.8 |
| Cumin (extra strong)....... | ................ | 13.6 | | | |
| Clove ("Eugenol")........ | Schimmel & Co. | 185.5 | Olibanum....... | Schimmel & Co.'s frankincense oil | 18.8 |
| Clove.......... | ................ | 152.5 | Parsley seed..... | Schimmel & Co. | 190.5 |

The above table gives the recorded methoxyl values, or mg. of alkyl in terms of methoxyl, present in one grm. of various oils. The majority of essential oils, however, contain no alkoxyl radical,

and hence give mere traces or no silver iodide when submitted to the process. Among these oils are those of absinthe, bergamot, bitter almonds (both natural and artificial), angelica, orange flowers, copaiba, coriander, cubebs, *Eucalyptus globulus*, Spanish, French, and African oils of geranium, juniper berries, cherry laurel, lavender, balm mint, lemon, peppermint, rosemary, sage, sandalwood, turpentine, and valerian.

The results of the examination of different samples of the same kind of oil did not invariably give the same results. Thus two samples of cumin oil gave small methyl values, whilst two others gave wholly negative results. Similar differences were observed with the oils of bergamot and citron-peel.

Benedikt and Grüssner point out that the method may be employed for the estimation of the eugenol in the oil of cloves, cinnamon, etc., and of anethol in the oils of anise and fennel. 235 parts of silver iodide precipitated correspond to 164 of eugenol, or 148 of anethol. It must be remembered, however, that such results include small quantities of other substances present containing methyl groups.

## Optical Activity of Essential Oils

The great majority of natural essential oils exercise a rotatory power on the plane of polarisation of light, and the optical activity may be ascertained quantitatively by the use of a polarimeter. The instrument employed should be one in which monochromatic light is used, saccharimeters constructed for observing the transition tint not being suitable for the purpose. The result of the observation commonly recorded is the angle of rotation observed when a column of oil 1 decimetre in length is traversed by the light. This may be conveniently called the "optical activity" of the oil. Sometimes this observation is calculated to the "specific rotatory power" of the sample by dividing the angle of rotation by the sp. gr. of the oil. Not a little confusion has arisen through observers' failing to state distinctly on what basis their results are expressed. In this volume all values for optical rotation are to be taken as referring to 100 mm. (1 decimetre) of the substance, unless otherwise specified. Optical activity may be denoted by the symbol $[\alpha]$, the specific rotatory power being expressed as $[\alpha]_D$.

The optical activity of an essential oil is one of the most valuable factors in its examination for purity, and this value is accentuated by optical observations on the fractions separated by distillation. Further, an observation of the optical activity of certain of the constituents of essential oils is a valuable criterion of the purity of the substances in question.

### Refractive Indices of Essential Oils

The determination of the refractive indices of essential oils is of considerable value in certain cases, but the figures given by a genuine oil and its adulterants frequently overlap each other to such an extent as to render the figure of little or no use. Still there are many instances in which the specific gravity and optical activity of an essential oil differ little from those of its common adulterants, and in these cases the determination of the refractive index will often give valuable information. Thus, oil of wintergreen has a high and nearly constant refractive index of about 1.5370 at 20°. Almost any adulterant will be directly detected by the determination of the refractive index of the sample. Sandalwood oil has also a high refractive index (about 1.5050 at 20°), and although adulteration with cedar-wood oil (refractive index, 1.500) could not be recognised by this method, the addition of castor oil would be readily detected.

Other useful applications of the determination will be made when its value is more generally recognised. The observation of the refractive index of the successive fractions yielded by a complex oil on distillation (preferably under reduced pressure), gives much sharper and more definite results than the observation of the index of the untreated sample. Thus, the terpenes have high refractive indices compared with the paraffins and their allies, and the presence of petroleum in essential oils may thus be ascertained. Sesquiterpenes, again, have a very high refractive index, and are thus easily detected in admixture with terpenes. Parry has in this manner recognised the presence of the oil of African copaiba in peppermint oil, and of resin spirit in citronella oil. Glyceryl acetate has also been detected in the residues on fractional distillation of an adulterated oil of peppermint. The very low refractive index at once suggested an open-chain compound.

A large number of determinations of the refractive index of various essential oils are recorded in a paper by Utz (*Apoth. Zeit.*, 1901, 742);

while H. G. Smith (*Proc. Roy. Soc., N. S. Wales,* 1906, **39**) has recorded the refractive indices of all the known eucalyptus oils (118 species), and based upon the figures obtained a classification of these oils into 7 groups.   Such a classification, however is extremely unscientific.

## Adulteration of Essential Oils

Essential oils are extremely liable to adulteration.   Scientific methods of adulteration are now largely practised, a type of the methods employed being the case of the addition of ethyl citrate or the acetic esters of glycerin to ester-containing oils, and so on. In addition to the above intentional adulterants, volatile oils are apt to contain water and resinous and other oxygenated substances produced by their exposure to air.

The proportion of *water* in essential oils is never very large.   The hydrocarbons in some cases dissolve about 1 : 1000, but in the oxygenated oils water is more soluble.   The presence of water may be detected by mixing 10 c.c. of the sample of oil, previously filtered if not perfectly clear, with 40 c.c. of petroleum spirit.   Any water will be separated in the form of minute globules, which, if in sufficient quantity, will ultimately coalesce and sink to the bottom of the liquid. On adding a small quantity of plaster of Paris, previously gently ignited and weighed, and agitating thoroughly, the water will be absorbed; and on filtering the liquid through dry paper, washing the plaster with a little anhydrous ether or very volatile petroleum spirit, and drying it at a gentle heat, the increase in its weight will represent the water in the 10 c.c. of the sample of oil employed. The petroleum spirit employed for the above test must be previously dehydrated by agitation with plaster of Paris.

**Alcohol** in essential oils may be detected by gradually adding some dry powdered calcium chloride, agitating well, and heating in a water-bath between each addition.   Mere traces of alcohol render the first portions of the calcium chloride pasty, but if present in larger proportions the salt dissolves and forms a heavy liquid layer. If the experiment be performed in a graduated tube, and a known measure of the oil employed, the diminution in its volume will give that of the alcohol mixed with it.   The calcium chloride should be added until it no longer dissolves in the heavier liquid. In testing for small quantities of alcohol by this test, the oil should

be previously dehydrated by agitating it with recently ignited plaster of Paris. Dragendorff recommends the use of metallic sodium, which does not act on hydrocarbons, and but slightly in the cold on oxygenated essential oils, if pure and dry; but in presence of 10 or even 5% of alcohol a brisk evolution of gas takes place. Aniline-red (magenta) is insoluble in essential oils, if pure and dry, but in presence of a small proportion of alcohol the oil acquires a pink or red colour. When the proportion of alcohol is considerable, fair quantitative results may be obtained by agitating the oil in a graduated tube with an equal measure of glycerin. The increase in the bulk of the latter liquid, measured after separation is complete, gives that of the alcohol (and water) in the sample examined. Simple agitation of the oil with water removes the alcohol sufficiently accurately for most purposes.

When the actual isolation of the alcohol is desired, E. Barbier recommends that one-tenth should be distilled off and the distillate saturated with an excess of dry potassium acetate, which forms with alcohol a heavy liquid. This is separated from the layer of oil, mixed with 4 times its volume of water, and again saturated with potassium acetate to get rid of the last traces of oil. The filtered aqueous liquid may then be distilled to one-half, when the alcohol will be found in the distillate.

**Chloroform** may be detected by dissolving the oil in alcohol and warming the liquid with zinc and dilute sulphuric acid. After some time several volumes of water are added, the aqueous liquid separated from the oil by passing it through a wet filter, and the filtrate tested for chloride by adding silver nitrate and nitric acid. A positive result proves the presence of chloroform in the oil. This substance is, however, rarely used to adulterate essential oils.

The detection and estimation of *alcohol* and *chloroform* in essential oils are rendered more delicate and accurate by previously distilling the sample, and applying the tests to the portion which passes over below 100°. A still better method is to pass a current of steam through the sample of oil contained in a small retort or tubulated flask. Any alcohol or chloroform will be found in the first portions of the distillate. On continuing the operation the essential oils distil over, though their b. p. are considerably above 100°; and after a time little or nothing but *resinous matters*, or *fixed oils* added as adulterants will remain in the retort. These may be weighed in the

retort, after heating it moderately and passing a current of coal-gas or air (previously filtered through cotton-wool) to separate any condensed steam and unvolatilised essential oils. The nature of the residue can then be ascertained by treating it with alcohol of 0.85 sp. gr. If wholly resinous it will dissolve, but fixed oils remain insoluble, with the exception of *castor oil*. To detect this, the alcoholic solution should be treated with an equal volume of sodium carbonate solution, and then boiled till the alcohol is driven off. Any *castor oil* will remain as an oily layer, but the *resin* will have dissolved in the alkaline liquid, and may be detected by separating any undissolved oil and acidulating with hydrochloric acid, when a turbid liquid will be formed from which resinous flocks or globules will gradually separate. In certain oils, however, a notable proportion of non-volatile stearoptene exists, such as in bergamot oil, which must not be confused with fixed matter added as an adulterant.

Oil of Turpentine is readily detected when present in essential oils by a fractional distillation of the sample, and examination of the fraction distilling about 160°. Pinene, the characteristic constituent of oil of turpentine, may then be recognised by its b. p., and by the characters of its nitroso-chloride, etc. In cases where pinene is a normal constituent of the oil, the physical characters of the lightest fractions of the oil will frequently give the clue to its purity or otherwise. The special methods for the detection of turpentine oil are given under the individual essential oils.

Another test for oil of turpentine and other adulterants of essential oils is founded on the solubility of the sample in alcohol, but as this is only a question of degree, and some of the more expensive oils closely simulate the behaviour of oil of turpentine itself, the inferences from the application of the test must be received with caution. Essentials oils differ considerably in their behaviour with alcohol, some undergoining solution much more readily than others. These differences are, of course, dependent on the composition of the oils, and hence will not be strictly constant for different samples of oil of the same kind.

Instead of observing the number of volumes of alcohol of a certain strength which are required to effect solution of an essential oil Dowzard suggests that 5 c.c. of the oil should be mixed with 10 c.c. of alcohol of 0.799 sp. gr. at 15°, and water then added gradually

from a burette until the liquid becomes turbid.    The end point is
stated to be very distinct, although some of the more readily soluble
oils show an opalescence before the liquid becomes distinctly turbid.
The volume of water in c.c. required to produce turbidity is
multiplied by 100, and the product termed the "solubility value"
of the oil.    Dowzard (*J. Soc. Chem. Ind.*, 1898, **17**, 1175) records
the solubility values, sp. gr., and optical rotation of various oils.

The following are the characters of the essential oils official in the
British Pharmacopœia (1914).

**Oleum Abietis** (oil of Siberian Fir; oil of Pine).—Oil of Siberian fir
is the oil distilled from the fresh leaves of *Abies sibirica*.    *Characters
and tests*.    Colourless or nearly so.    Aromatic odour: taste pungent.
Specific gravity 0.900 to 0.920 at 15.5°; optical rotation, $-32°$ to $-42°$;
refractive index at 25° about 1.4740.    Contains 30 to 40 per cent. of
esters calculated as bornyl acetate, $C_{10}H_{17}C_2H_3O_2$.

**Oleum Ajowan** (Ajowan oil: Ptychotis oil).—Ajowan oil is the
oil distilled from the fruit of *Carum copticum*.    *Characters and tests*.
Colourless with an odour and taste resembling thyme.    Specific
gravity 0.910 to 0.930 at 15.5°; optical rotation $+1°$ to $+2°$.    When
10 millilitres with 100 millilitres of solution of sodium hydroxide in a
flask with a narrow graduated neck are heated on a water bath, well
shaken, and allowed to stand, the uncombined oil, cooled to 15.5°
measures not more than 6 millilitres (presence of not less than 40
per cent. of thymol).

**Oleum Anethi** (oil of Dill).—Oil of Dill is the oil distilled from
Dill fruit.    *Characters and tests*.    Colourless or pale yellow, darkening
on keeping; odour that of Dill fruit; taste at first sweet and aromatic,
but subsequently pungent.    Specific gravity 0.900 to 0.915 at 15.5°;
optical rotation $+70°$ to $+80°$; refractive index at 25° 1.483 to 1.488.
Soluble in 3 parts of alcohol (90 per cent.).

**Oleum Anisi** (oil of Anise).—Oil of Anise is the oil distilled from
Anise fruit; or from the fruit of the star-anise, *Illicium verum*.
*Characters and tests*.    Colourless or pale yellow.    Odour that of anise
fruit; taste sweet and aromatic.    Specific gravity at 20° (compared
with water at 15.5°) 0.975 to 0.990; optical rotation $-2°$ to $+1°$;
refractive index at 25° 1.552 to 1.558.    Congeals when stirred at
about 15.5°; and does not again liquefy below 17°.    Not less than
80 per cent. distils between 225° and 235°.    Soluble in 3 parts of
alcohol (90 per cent.).

**Oleum Anthemidis** (oil of Chamomile).—Oil of Chamomile is the oil distilled from chamomile flowers. *Characters and tests.* Blue when freshly distilled, but gradually becoming greenish or brownish-yellow under the influence of air and light. Odour that of chamomile flowers; taste aromatic, characteristic. Specific gravity 0.905 to 0.915 at 15.5°; optical rotation −1° to +3°; refractive index at 25° about 1.445. Soluble in less than 1 part of alcohol (90%).

**Oleum Cajupti** (oil of Cajuput).—Oil of Cajuput is the oil distilled from the leaves of Melaleuca leucadendron and other species of Melaleuca. *Characters and tests.* Green or bluish-green. Agreeable camphoraceous odour; taste aromatic, bitter and camphoraceous. Specific gravity 0.919 to 0.930; optical rotation not more than −4°; refractive index at 25°, 1.460 to 1.467. When 10 millilitres of the oil are mixed with 4 to 5 millilitres of syrupy phosphoric acid in a vessel surrounded by a freezing mixture, and then pressed strongly in a piece of fine calico between folds of blotting paper, the pressed cake, decomposed by warm water in a graduated vessel yields an oily layer which on cooling to 15.5° measures not less than 4.5 millilitres (presence of not less than 45 per cent. of cineol).

**Oleum Carui** (oil of Caraway).—Oil of caraway is the oil distilled from caraway fruit and rectified. *Characters and tests.* Colourless or pale yellow; odour and taste those of caraway fruit. Specific gravity 0.910 to 0.920 at 15.5°; optical rotation +75° to +82°; refractive index at 25°, 1.485 to 1.497. Soluble in 1 part of alcohol (90 per cent.) and in 10 parts of a mixture of equal volumes of alcohol (90 per cent.) and alcohol (70 per cent.). When fractionally distilled at the rate of one drop per second, not less than 50 per cent. distils at a temperature above 200°.

**Oleum Caryophylli** (oil of Cloves).—Oil of cloves is the oil distilled from cloves. *Characters and tests.* Colourless or pale yellow when fresh, darkening with age and on exposure to air. Odour and taste those of cloves. Specific gravity 1.047 to 1.065 at 15.5°; refractive index at 25° 1.528 to 1.540. Soluble in 3 parts of alcohol (90 per cent.), the solution yielding a blue colour with ferric chloride solution. When 10 millilitres of the oil are well shaken with 100 millilitres of solution of sodium hydroxide, heated on a water bath in a flask with a narrow graduated neck, and then allowed to stand, the uncombined oil, cooled to 15.5°, measures not more than 1.5 millilitres (presence of not less than 85 per cent. of eugenol).

**Oleum Cinnamomi** (oil of Cinnamon).—Oil of cinnamon is the oil distilled from cinnamon bark. *Characters and tests.* Yellow when freshly distilled, gradually becoming reddish. Odour and taste those of cinnamon bark. Specific gravity 1.000 to 1.030 at 15.5°; optical rotation −0.5° to −1°; refractive index at 25° 1.565 to 1.580. Soluble in from 3 to 4 parts of alcohol (70%). 1 drop dissolved in 5 millilitres of alcohol (90%) assumes a pale green, but not a blue or brown coloration, on the addition of 1 drop of solution of ferric chloride (absence of cinnamon leaf oil and cassia oil). Contains from 55 to 65 per cent. of cinnamic aldehyde as determined by the following test:

To 10 millilitres of the oil add 70 millilitres of an aqueous solution (1 in 5) of sodium sulphite and sufficient solution of phenolphthalein to give a well marked pink coloration. Heat the mixture on a water bath, shake well, and neutralise with acetic acid diluted with twice its volume of water; repeat the heating and neutralisation until no further pink coloration is developed, the time occupied being from thirty to forty-five minutes. The oily layer which separates on standing, cooled to 15.5°, measures not more than 4.5 or less than 3.5 millilitres (presence of 55 to 65 per cent. of cinnamic aldehyde).

**Oleum Copaibæ** (oil of Copaiba).—Oil of Copaiba is the oil distilled from Copaiba. *Characters and tests.* Colourless or pale yellow. Odour and taste, those of copaiba. Specific gravity 0.896 to 0.910 at 15.5°; optical rotation −7° to −35°; refractive index at 25° 1.494 to 1.500. Distils between 250° and 275°. A solution of 1 millilitre of the oil in 5 millilitres of glacial acetic acid does not develop more than a faint violet coloration on the addition of 4 drops of nitric acid (absence of gurjun oil). When distilled in a vacuum, the first 10% of the distillate has an optical rotation lower than that of the original oil (absence of oil of African Copaiba).

**Oleum Coriandri** (oil of Coriander).—Oil of Coriander is the oil distilled from coriander fruit. *Characters and tests.* Colourless or pale yellow. Odour and taste those of coriander fruit. Specific gravity 0.870 to 0.885 at 15.5°; optical rotation +8° to +14°; refractive index at 25° 1.4630 to 1.4670. Soluble in 3 parts of alcohol (70 per cent.).

**Oleum Cubebæ** (oil of Cubebs).—Oil of Cubebs is the oil distilled from cubebs. *Characters and tests.* Colourless, pale green or greenish-yellow. Odour and taste those of cubebs. Specific gravity 0.910 to 0.930 at 15.5°; optical rotation −25° to −40°; refractive index

at 25° 1.4860 to 1.5000. Not less than 60 per cent. distils between 250° and 280°.

**Oleum Eucalypti** (oil of Eucalyptus).—Oil of Eucalyptus is the oil distilled from the fresh leaves of *Eucalyptus globulus*, *Eucalyptus dumosa* and other species of Eucalyptus, and rectified. *Characters and tests*. Colourless or pale yellow. Aromatic, camphoraceous odour; taste pungent, leaving a sensation of cold. Specific gravity 0.910 to 0.930 at 15.5°; optical rotation −10° to +10°. Soluble in 5 parts of alcohol (70%). Contains not less than 55% by volume of cineol as estimated by the process described under oleum cajupti. When 1 millilitre is mixed with 2 millilitres of glacial acetic acid and 5 millilitres of petroleum spirit, 2 millilitres of a saturated aqueous solution of sodium nitrite being added, and the mixture gently shaken, no crystalline precipitate forms in the upper layer (absence of oils containing much phellandrene).

**Oleum Gaultheriæ** (oil of Gaultheria; oil of Wintergreen).—Oil of gaultheria is the oil distilled from the leaves of *Gaultheria procumsens*, or from the bark of *Betula lenta*. *Characters and tests*. Colourless or nearly colourless. Strong, characteristic odour; taste pungent. Specific gravity 1.180 to 1.187 at 15.5°; optical rotation 0° to −1°; refractive index 1.5370 to 1.5390 at 25°. Soluble in 6 parts of alcohol (70%) at 25°. Contains not less than 99% of esters calculated as methyl salicylate $CH_3.C_7H_5O_3$.

**Oleum Graminis Citrati** (oil of Lemon Grass).—Oil of lemon grass is the oil distilled from *Cymbopogon citratus* and *Cymbopogon flexuosus*. *Characters and tests*. Dark yellow. Odour resembling that of verbena. Specific gravity 0.880 to 0.905 at 15.5° optical rotation −3° to +3°. Contains not less than 70% of aldehydes as estimated by the process decribed under oleum cinnamomi.

**Oleum Juniperi** (oil of Juniper).—Oil of Juniper is the oil distilled from the ripe fruit of *Juniperus communis*, and rectified. *Characters and tests*. Colourless or pale yellowish-green. Odour that of the fruit; taste warm, aromatic and bitter. Specific gravity 0.862 to 0.890, at 15.5° increasing with age; optical rotation −3° to −15°; refractive index at 25° 1.4720 to 1.4880 at 25°. Soluble when freshly distilled in 4 parts of a mixture of equal volumes of alcohol (90%) and absolute alcohol, becoming less soluble with age.

**Oleum Lavandulæ** (oil of Lavender).—Oil of lavender is the oil distilled from the flowers of *Lavandula vera*. *Characters and tests*.

Pale yellow or yellowish-green. Odour that of the flowers. Taste pungent, slightly bitter. Specific gravity 0.883 to 0.900 at 15.5°; optical rotation $-3°$ to $-10°$. Soluble in 4 parts of alcohol (70%). Contains from 7 to 11 per cent. of esters (English oil) or not less than 30% of esters (foreign oil) calculated as linalyl acetate, $C_{10}H_{17}C_2H_3O_2$.

**Oleum Limonis** (oil of Lemon).—Oil of Lemon is the oil obtained from lemon peel by various methods of expression. *Characters and tests.* Pale yellow, volatile; odour that of lemons; taste warm, afterwards slightly bitter. Specific gravity 0.857 to 0.860 at 15.5°; optical rotation $+58°$ to $+64°$; refractive index at 25°, 1.4730 to 1.4760. Contains not less than 4 per cent. by weight of aldehydes, calculated as citral $C_{10}H_{16}O$, as estimated by the following process: To 20 grammes of the oil contained in a flask add 20 millilitres of $N/2$ solution of hydroxylamine hydrochloride, 8 millilitres of $N/1$ alcoholic solution of potassium hydroxide, and 20 millilitres of alcohol (90%). Attach a reflux condenser, boil for thirty minutes, cool, and dilute with 250 millilitres of water, rinsing the condensing tube into the flask with part of this quantity. Neutralise the solution thus obtained with $N/1$ alcoholic solution of potassium hydroxide, solution of phenolphthalein being used as indicator, and then titrate with $N/2$ solution of sulphuric acid, solution of methyl orange being used as indicator. Repeat the experiment, omitting the oil of lemon. The quantity of $N/2$ solution of sulphuric acid required in the second experiment exceeds that required in the first experiment by not less than 10.5 millilitres (presence of not less than 4% of aldehydes, calculated as citral $C_{10}H_{16}O$).

**Oleum Menthæ Piperitæ** (oil of Peppermint).—Oil of peppermint is the oil distilled from fresh flowering peppermint, *Mentha piperita,* and rectified, if necessary. *Characters and tests.* Colourless, pale yellow or greenish yellow. Odour that of peppermint herb; taste pungent and aromatic followed by a sensation of cold. Specific gravity 0.900 to 0.920 at 15.5°; optical rotation $-20°$ to $-35°$. Soluble in 4 parts of alcohol (70 per cent.). Contains not less than 50 per cent. of total alcohols, free and combined, calculated as menthol, $C_{10}H_{20}O$, and not less than 5% of esters, calculated as menthyl acetate, $C_{10}H_{19}.C_2H_3O_2$.

**Oleum Menthæ Viridis** (oil of Spearmint).—Oil of spearmint is the oil distilled from fresh flowering spearmint, *Mentha viridis,* or *Mentha crispa. Characters and tests.* Colourless, pale yellow, or

greenish-yellow, becoming darker on keeping. Odour and taste those of spearmint herb. Specific gravity 0.925 to 0.940 at 15.5°; optical rotation −20° to −50°. Soluble in 3 parts of alcohol (90%). Forms a clear solution with 1 part of equal volumes of alcohol (90%) and alcohol (70%), the solution becoming turbid on further dilution.

**Oleum Myristicæ** (oil of Nutmeg).—Oil of Nutmeg is the oil distilled from nutmeg, and rectified. *Characters and tests*. Colourless or pale yellow. Odour and taste those of nutmeg. Specific gravity 0.870 to 0.925 at 15.5°; optical rotation +13° to +30°; refractive index at 25°, 1.4740 to 1.4840. Soluble in 3 parts of alcohol (90%). Leaves not more than 5% of residue when evaporated on a water bath.

**Oleum Rosæ** (oil of Rose; otto of Rose).—Oil of Rose is the oil distilled from the fresh flowers of *Rosa damascena*. *Characters and tests*. A pale yellow, or yellowish-green cyrstalline mass, semi-solid at ordinary temperatures. Strong, fragrant, rose like odour; taste sweetish. Specific gravity at 30° (compared with water at 15.5°) 0.854 to 0.862; optical rotation − 2° to −4°; refractive index at 25°, 1.4560 to 1.4650; melting point 20° to 23°.

**Oleum Rosmarini** (oil of Rosemary).—Oil of Rosemary is the oil distilled from the flowering tops of *Rosmarinus officinalis*. *Characters and tests*. Colourless or pale yellow. Odour that of rosemary; taste warm, camphoraceous. Specific gravity 0.895 to 0.920; at 15.5°; optical rotation −2° to +15°; refractive index at 25°, 1.4630 to 1.4730. Soluble in 1 part of alcohol (90 per cent.) and in 5 to 10 parts of a mixture of equal volumes of alcohol (90 per cent.) and alcohol (70%). Contains not less than 10% of total alcohols, calculated as borneol $C_{10}H_{18}O$, and not less than 1.8 per cent. of esters, calculated as bornyl acetate, $C_{10}H_{17}C_2H_3O_2$.

**Oleum Santali** (oil of Sandalwood).—Oil of Sandalwood is the oil distilled from the wood of *Santalum album*. *Characters and tests*. Pale yellow or nearly colourless, somewhat viscid in consistence. Aromatic odour; taste unpleasant. Specific gravity 0.973 to 0.985 at 15.5°, optical rotation −13° to −21°; refractive index at 25°, 1.4980 to 1.5080. Soluble in 6 parts of alcohol (70%) at 20°. Contains not less than 90% of total alcohols, calculated as santalol $C_{15}H_{24}O$.

**Oleum Sinapis Volatile** (volatile oil of Mustard).—Volatile oil of mustard is the oil obtained by distillation from black mustard

seeds, deprived of most of their fixed oil and macerated in water for several hours. *Characters and tests*.   Colourless or pale yellow. Intensely penetrating odour.   Produces almost immediate vesication when applied to the skin.   Specific gravity 1.014 to 1.025 at 15.5°. Distils between 148° and 156°.   Contains in 100 millilitres not less than 92 grammes of allyl isothiocyanate, $C_3H_5NCS$, as determined by the following process:

With alcohol (90 per cent.) prepare a solution containing a 1 grm. of the oil in 50 millilitres.   To 5 millilitres of this solution in a 100 millilitre flask add 30 millilitres of N/10 solution of silver nitrate and 5 millilitres of solution of ammonia.   Heat on a water bath to 80° for thirty minutes, shaking frequently; cool to 15.5°, make up to exactly 100 millilitres with water, and filter.   To 50 millilitres of the filtrate add 4 millilitres of nitric acid, a few drops of solution of ferric sulphate, and sufficient N/10 solution of ammonium thiocyanate to produce a permanent red colour.   Not more than 5.7 millilitres of the latter reagent are required (presence of not less than 92 grammes of allyl isothiocyanate in 100 millilitres of the oil).

**Oleum Terebinthinæ Rectificatum** (rectified oil of Turpentine).— Rectified oil of turpentine is the oil distilled from the oleo-resin (turpentine) obtained from various species of Pinus, and rectified. *Characters and tests*.   A colourless, limpid liquid.   Characteristic odour; taste pungent, somewhat bitter.   Specific gravity 0.860 to 0.870 at 15.5°; refractive index at 25°, 1.4650 to 1.480.   Distils almost entirely between 156° and 180°, leaving no appreciable residue.

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